SCHOOL OF
CIVIL ENGINEERING

INDIANA
DEPARTMENT OF HIGHWAYS

JOINT HIGHWAY RESEARCH REPORT

FHWA/IN/JHRP-85/8

SELECTION AND USE OF FLY ASH FOR HIGHWAY CONCRETE

FINAL REPORT

Sidney Diamond

PURDUE UNIVERSITY

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TO: H. L. Michael, Director
Joint Highway Research Project

May 16, 1985
Revised: September 9, 1985
Project C-36-19F

FROM: Sidney Diamond, Research Associate
Joint Highway Research Project

File: 5-5-6

Attached is the Final Report of Phase I of the HPR Part II Study titled "Selection and Use of Fly Ash for Highway Concrete." The Report carries the same title, and has been authored by the principal investigator, Professor Sidney Diamond.

The objectives of the Study were accomplished. A suite of representative Indiana fly ashes was selected, sampled from the power plants, and tested in great detail to provide information on the properties of these individual fly ashes and on expected properties of the range of fly ashes that are available for potential use in highway concrete in the various regions of the state.

This Final Report is forwarded for review and acceptance by all sponsors as fulfilling the objectives of the study. With its approval and subsequent publication the Phase I referenced HPR study will have been completed. A proposal for a projected Phase II study in which a smaller group of fly ashes is tested extensively in appropriately designed highway concrete mixes has been approved by the Board and forwarded to IDOH and FHWA for their consideration.

Respectfully submitted,

Sidney Diamond, HLM

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16. Abstract

A suite of representative Indiana fly ashes was selected and sampled from power stations in all parts of the state, and tested to provide background information for selection and use of fly ash in highway concrete. Tests included complete chemical analyses and determination of soluble alkalies and sulfate; particle size distribution; surface area and specific gravity measurements; determination of content of magnetic (non-reactive) particles; x-ray diffraction; scanning electron microscope study; and determinations of pozzolanic activity index. It was found that most Indiana fly ashes were Class F materials, only two Class C fly ashes being among those sampled. Many of the Class F fly ashes were almost identical in chemical analyses parameters, apparently due to their common origin in local Illinois Basin coals. There were major differences among the fly ashes in carbon contents, particle size distributions, and other properties of importance with respect to prospective use of fly ash in highway concrete.

Several new laboratory techniques useful in the study of fly ash and similar materials were developed in the course of this work.

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Fly ash, testing, chemical analysis, particle size, specific gravity, surface area, x-ray diffraction, scanning electron microscopy, pozzolanic activity index, concrete

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SELECTION AND USE OF FLY ASH FOR HIGHWAY CONCRETE

by

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for

Indiana Department of Highways

and

Federal Highway Administration
U. S. Department of Transportation

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A number of people have contributed very materially to this work, which represents something of a collective effort. Some of the fly ashes were collected by Prof. D. N. Winslow and by Mr. F. Lopez Flores, although most were collected by the writer. By far the greater portion of the various laboratory determinations was carried out by Miss Carol Kilgour. These included the total chemical analyses, the color measurements, the particle size measurements, the surface area determinations, the specific gravity measurements, the determination of magnetic particle content, the acquisition of most of the x-ray diffraction patterns, and the pozzolanic index testing. Prof. W. L. Dolch suggested and set up the scheme for total chemical analysis, and monitored the results. The LECO analyses of carbon and sulfur were done by Mrs. Janet Lovell. Determinations of surface area and specific gravity were set up and supervised by Prof. Winslow. Some of the x-ray diffraction work, and invaluable assistance in various laboratory procedures throughout the project were provided by Mrs. Lovell. The writer is deeply grateful to all of these colleagues.

The writer also wishes to express his gratitude to the executives and station personnel of the various electrical utilities who were invariably cooperative and helpful in providing authorization and facilitating the sampling of fly ash from the different generating stations. These include the Northern Indiana Public Service Company,

the Indianapolis Power and Light Company, Public Service Indiana, Southern Indiana Gas and Electric Company, Indiana Michican Electric Company, and the Richmond Power and Light Department. The cooperation of the American Fly Ash Company and the Michigan Ash Sales Company are also acknowleged with thanks.

HIGHLIGHT SUMMARY

This project was designed to provide a basic understanding of the potential sources of fly ash available for use in highway concrete in the state of Indiana.

A relatively large number of coal-burning power plants exist in Indiana since there are no active nuclear or hydro power facilities. Their locations are not uniformly distributed however; there are many plants in the coal-mining regions of southern Indiana and along the Ohio River, but essentially no sources of fly ash in northeastern Indiana.

A total of 14 fly ashes were collected, including twelve from within the state and two from southwestern Michigan that are marketed commercially in northeastern Indiana; the assemblage provided reasonable coverage of the state. The plants sampled ranged in size from 45 MW to over 2500 MW rated capacity, and included at least one from each of the five operating utilities in the state.

The fly ashes were examined in great detail using both standard and a number of special characterization methods. The color of each fly ash was determined according to the standard Munsell color naming system. Chemical methods included total chemical analyses, carbon analyses by the LECO method, and analyses of soluble alkalies and sulfates. Particle size distributions were determined and plotted graphically, along with measurement of mean particle size and percentage larger than 45 μm. Surface areas were measured several different ways, as were the specific gravities of the fly ashes. The contents of magnetic particles of each ash were measured, and x-ray diffraction analysis was carried out both

for the whole fly ash and for the separated magnetic fraction. Scanning electron microscope characterization of each ash was provided. The pozzolanic activity index with cement was determined for each fly ash by both the standard method and a modified method.

All but two of the fly ashes were Class F low-calcium materials. Most had very similar chemical characteristics which reflected their derivation from fairly uniform Illinois Basin coals; four were significantly different in chemistry. The fly ashes derived from Illinois Basin coals had high iron contents, and correspondingly high percentages of magnetic particles. The magnetic fractions generally were composed of components that are not reactive with cement, and should be classed as additions to the fine aggregate rather than as replacements for the cement.

The carbon contents of the fly ashes examined covered a wide spectrum, from less than 0.5% to about 9%. Particle size distributions also varied considerably; the finest fly ash had a mean size of only 3μm, the coarsest 78μm.

The two Class C fly ashes tested were both of high CaO contents (ca. 30%), but differed from each other in a number of properties.

Most of the fly ashes would seem to be at least marginally useful in concrete; one apparently highly superior ash and one very coarse ash that would be useless in concrete were also among the collection.

In carrying out this work, new methods of determining the content of magnetic particles, of mounting fly ash for scanning electron microscopy examination, and of displaying particle size distribution results were developed that should be of general utility.

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INTRODUCTION

The use of fly ash in concrete, including concrete for highway pavements, has become widespread in the U.S. and in many other countries in recent years. As attested in a large number of technical reports and symposia devoted to the subject, such use can confer benefits of several kinds: economic, in that fly ash can be used to partly replace portland cement in concrete at a substantially lower unit cost; and technical in that workability, eventual strength, and durability of the concrete can be improved.

The economic benefit is immediate, and does not depend on the fly ash selected, as long as its effect in the concrete is not deleterious. The technical benefits are not generally immediate (except for improvement in workability), and their realization in practice depends on selecting a specific fly ash for use that is physically and chemically capable of providing the combination of characteristics needed, and in designing the concrete mix to take advantage of the presence of the fly ash.

Fly ashes vary significantly in properties, depending on the nature of the coal being burned, the efficiency of the coal grinding, combustion, and fly ash collection processes, and any treatment applied during or after recovery. Detailed knowledge of the characteristics of fly ashes is not common among civil engineers and concrete technologists; indeed, the managers and engineers who design and operate coal-burning power plants that produce fly ash typically know little about it.

For a number of years it has been the policy of the Federal Highway Administration (FHWA) to encourage the use of fly ash in highway

pavement and structural concrete, in view of the benefits that may be obtained, and also to help mitigate possible environmental effects of non-utilization and consequent dumping of the material. Recently it has been mandated that all State highway and transportation departments be required to permit the use of fly ash in highway concretes as an optional bid item at the option of the contractor.

Unfortunately, many State highway agencies have little or no direct experience with selection and use of fly ash in highway concrete. Indeed in many areas little information is available on the range of properties of fly ashes that may be available locally. Fly ash, being a relatively high volume, low unit value bulk product, cannot be economically transported long distances. Except in special circumstances, if fly ash is to be used at all, it must be produced at distances no more than several hundred miles from the point of use.

While such restrictions also apply to other concrete and highway materials, notably aggregates, the properties and behavior of the latter are generally well known and do not cause much concern to highway agencies and other concrete users. If aggregates are frost resistant, sound and appropriately sized, and not alkali reactive, they may generally be used from local sources without too much concern for details of variation in composition and physico-chemical behavior. Fly ash, being an active chemical component in the concrete mix, requires much more concern.

In contrast to some states, the state of Indiana has a large number of coal-burning electrical power plants actively producing fly ash. Nearly all of the electrical power produced in this state is derived from coal; there are no substantial numbers of hydroelectric or nuclear power

producing plants in operation.

Five commercial electrical utilities are franchised to produce electrical power in the different regions of the state. In addition there are a number of municipal and smaller privately-owned plants. Other utilities operate coal-burning power plants in adjacent areas of the surrounding states of Kentucky, Ohio, Michigan, and Illinois that might generate fly ash that could be used in highway concrete within Indiana. The total number of different potential sources is estimated at somewhere between 35 and 50 different plants. This is in marked contrast to some states which may have as few as four or five possible sources.

Comparatively little is known about the characteristics of the fly ashes being produced in Indiana. There is no compilation of the possible sources, let alone the properties of the fly ashes being produced. What little information is available on fly ash properties within the state is mostly the result of testing by the several fly ash brokers active in the state, and refers only to the ashes that they market.

Technical standards for the selection of fly ashes for use in concrete exist; ASTM C 618 can be used as an acceptance standard for fly ash in concrete. However, realistically, it is the common consensus among those familiar with such matters that these standards in their present form are inadequate and badly set up. Efforts to suggest revisions and more appropriate criteria have been made from time to time, and are frequent subjects for papers and discussions at technical meetings. Unfortunately, there is little agreement as to the specifics of the changes that should be made, owing in part to inadequate information on the actual behavior of fly ash in concrete, and in part to commercial considerations.

The present work was undertaken in the light of all of these

circumstances to provide a needed body of information on the physical and chemical characteristics of the fly ashes currently being produced in Indiana. It is not complete, in that only a representative group of fly ash sources, rather than the total of all of the plants now actively burning coal, was selected. The sampling methodology itself was less than ideal, being constrained by practical consideration of where a sample could be taken from a given plant. It was also not possible to do repeat sampling, desirable as that would have been.

Nevertheless, the fly ash samples were personally secured, in all but three cases, by a staff member of the project, and once secured was carefully transported, stored, handled, and subsampled. Each of the fly ashes was subjected to extremely rigorous and thorough evaluation and characterization procedures, including a number of original techniques and others not original but not generally used in the fly ash industry. The present work constitutes a compilation of information on properties of locally-available fly ashes that the writer believes to be unique in the U.S. and probably the world.

This work is conceived as being only the first part of a more extensive research effort. The present work was confined to the study of the characteristics of the fly ashes themselves. A proposal is pending to continue the research by selecting a smaller suite of representative fly ashes and studying their behavior and the effects produced in optimally-designed highway pavement and structural concrete.

SELECTION AND SAMPLING OF FLY ASH SOURCES

Selection of the specific plants to be sampled as potential sources of fly ash for this project was a fairly complicated task. It was realized at the start of the project that it would be impractical to sample fly ash generated at every coal burning power station in the state, and that criteria for selection needed to be established.

It was decided at the beginning of the project that whether or not the ash was currently being marketed commercially would not be one of the criteria employed. These change over a period of time, and we wanted to be in a position to examine a representative selection of Indiana fly ashes regardless of whether or not they were currently being sold commercially.

One of the obvious criteria we did employ was geographical. It was naturally desired to sample representative stations in each of the regions of the state. Even this was not a simple task, since coal burning power stations are not spread uniformly throughout the state. There is a high concentration in the extreme southern part, especially along the Ohio River, where transportation of coal is inexpensively accomplished. In contrast, northeastern Indiana is essentially without power stations.

In the final tally, among the 14 fly ashes chosen for study a reasonable geographic balance was reached, with 3 fly ash sources identified as being from northwestern Indiana, 4 from central Indiana, 3 from southwestern Indiana, 2 from southeastern Indiana, and the remaining two from adjacent southwestern Michigan. The latter two are fly ashes that are commercially "imported" for sale and use in northeastern Indiana and were sampled in lieu of available fly ash sources within that part of the

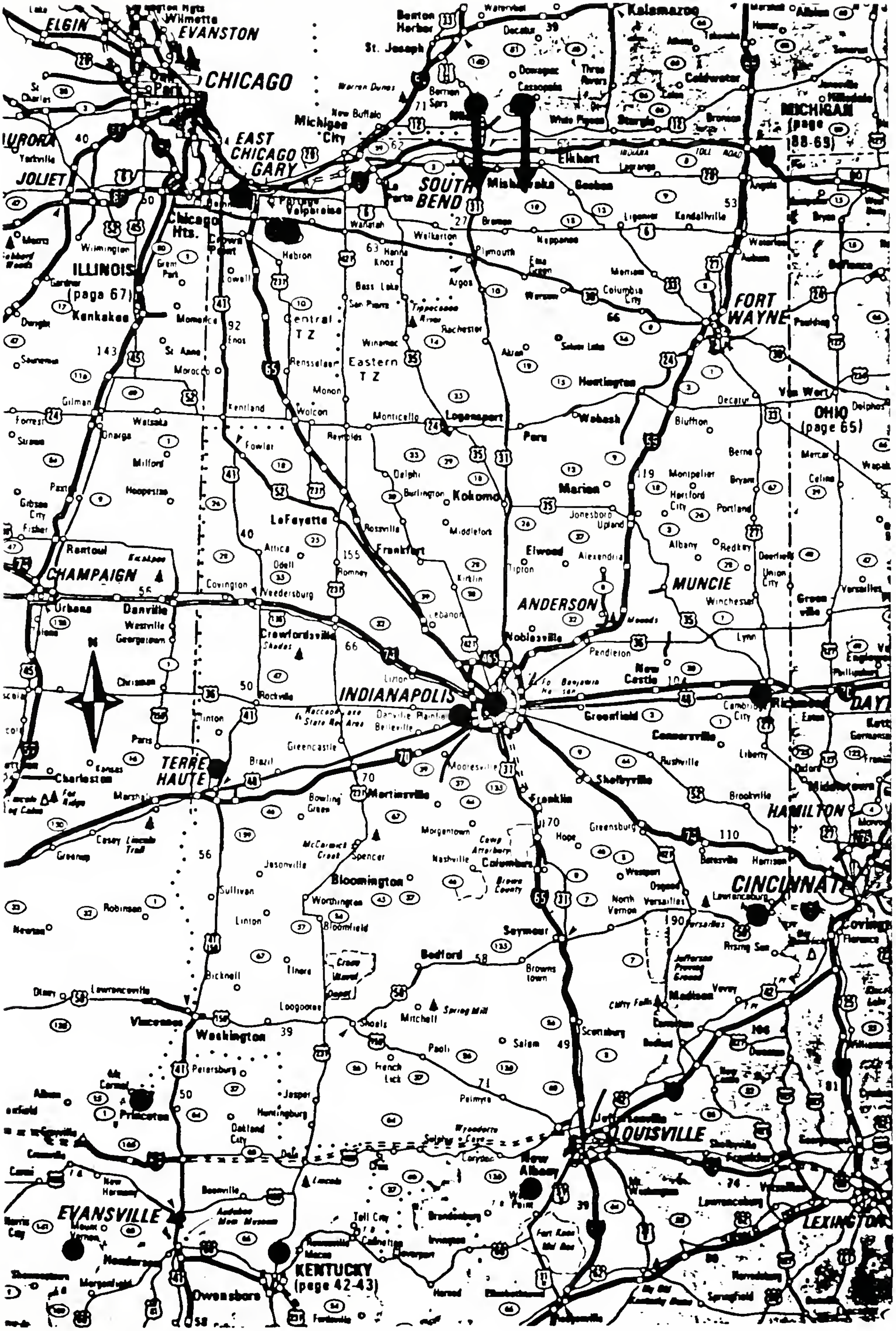
state.

A map indicating the general location of each of the sources is provided in the accompanying figure.

Another criterion for selection was with respect to the utility companies. It was desired to include fly ash from at least one generating station operated by each of the franchised power utilities operating in the state, and also fly ash from at least one municipal power station. This was accomplished; the final collection includes 3 fly ashes from stations of the Northern Indiana Public Service Co. (NIPSCO), 2 from the Indianapolis Power and Light Co. (IPALCO), 3 from Public Service Indiana (PSI), 2 from Southern Indiana Gas and Electric Co. (SIGECO), and from Indiana and Michigan Electric Co. (IME). In addition, one of the Michigan fly ashes was produced by an electric utility in Michigan (Consumer Power Co). The remaining two fly ashes were produced in municipal-owned power stations, one in Richmond, Indiana, and the other in Lansing, Michigan.

Still another criterion for selection was the desire to have representation from all sizes of generating stations, from the smallest to the largest. This was accomplished reasonably well, the stations sampled ranging from the 45 MW rated Perry K. Station of IPALCO in Indianapolis to the 2540 MW Gibson Station of PSI in Gibson County, Indiana, the latter the largest operating within the state.

Finally, a very important criterion was the practicality of conducting the sampling itself. On this we were necessarily guided by the advice and information supplied by the executive in charge of fly ash collection and disposal for each utility. For various reasons it simply was impractical to collect samples from some of the plants that we might otherwise have desired to sample. It should be recorded here that these were always



Map Showing Approximate Locations of Fly Ash Sources Within Indiana
(Note: Location of the Two Michigan Fly Ashes Only Schematic)

technical or physical reasons; all of the representatives of the utilities we contacted in making the necessary arrangements were unfailingly helpful and courteous in the extreme, as were the utility employees who actually helped us with the sampling operation.

Unfortunately, fly ash collection and disposal systems are closed air-transport materials handling systems, many of which are not equipped with sampling ports at convenient locations. We often had little choice in terms of where the sample collected actually came from; in many stations we were constrained to sample individual hoppers, which may or may not have been fully representative of the overall output. This was especially a problem where the fly ash was not being collected in silos for storage or marketing purposes, but was being blown directly into ash ponds, without any opportunity for collection en route.

The actual collection on site was made into plastic bag-lined new plastic trash cans equipped with tight fitting lids. Samples approximating 100 lbs. were secured from each site. There were a few problems with warm fly ash, but basically this procedure worked well. Each sample was properly tagged both in and on the outside of the container, brought back to the laboratory, and carefully stored in a designated and controlled area for subsampling and reference storage.

FLY ASH PRODUCTION REPRESENTED

Before proceeding to the details of the characterization of the individual fly ashes, it is appropriate to consider something of the magnitude of the production of fly ash represented by the sampling program.

No accurate figures exist for the total annual production of fly ash within the state, although the National Ash Association does compile such figures on a national basis.

It is possible to form some idea of the volume of fly ash produced by the plants sampled in this program. When actually doing the sampling, information was requested from each plant supervisor or his representative as to the actual annual production of fly ash from his plant. However, estimates were obtained only from 7 of the 14 plants sampled. In an effort to develop a relationship between plant generating capacity (MW) and fly ash production, the estimated annual fly ash tonnage for each plant was divided by its rated capacity to derive a value for annual tonnage per MW. These varied, but averaged 240 tons per year per MW capacity for the seven plants. These plants varied in capacity from about 100 to about 1,000 MW.

Assuming that this average could be applied generally, the 14 plants sampled, with a total rated capacity of approximately 9,000 MW, would be expected to generate a total of approximately 1,700,000 tons of fly ash per year. If these calculations are at all accurate, it certainly appears that far more fly ash is being generated than can possibly be used in highway or other concrete construction in Indiana. This being the case, it is obvious that a factor of selectivity is

entirely warranted; that is, only fly ash that can be expected to perform in a relatively superior manner in such concrete should be used.

METHODS OF EXAMINATION

Introduction

Determination of the properties of fly ashes relevant to their potential usage and performance in concrete is not a straightforward task. The few standardized procedures used in ASTM C 618 are far from adequate to properly characterize the important properties of fly ash as a material for use in concrete.

In this work a large number of diverse laboratory measurements, many of them beyond the capabilities of most laboratories dealing with fly ash, were used to develop a synthesis - an overall profile of the characteristics of each ash.

In measuring some of the parameters, for example specific gravity, several different methods were used. Thus a set of parallel measurements of the same material by three or four different procedures was obtained. When such alternate procedures gave the same or almost the same results, enhanced confidence in the correctness of the value resulted. When they did not, or more commonly, did for some fly ashes and did not for others, useful leads could be developed as to why they differed for the specific samples in which differences were found. Such leads provide clues as to the nature of the materials themselves that might otherwise be missed, and thus further the progress of research in understanding the behavior of these complex substances.

Descriptions of each of the specific methods used are provided below.

Color

The international standard method for the expression of color on a numerical scale, as adopted by the National Bureau of Standards, the paint industry, the dye industry, and many international agencies, is the Munsell color system. In this system a sample of the material is compared with a series of standard color chips to get a closest available match. The "color" of the resulting match is expressed in quantitative terms in values of three parameters: hue, which represents its positioning on the red-yellow-green-blue-purple color wheel; value, which indicates the position on a white-gray-black scale; and chroma, which indicates color strength or saturation, i.e. the degree of departure from the white-gray-black center to the periphery of the color wheel where the colors are "pure". In the standard notation the color designation is first the hue parameter (for example 5Y or 10 YR), followed by a space, then the value parameter (on a scale from 1 black to 10 white), and finally a slash and then the chroma number (on a scale from 0 (very weak, i.e black or white to 20 (pure intense color). A set of verbal equivalents is designated by convention. While there is no standard set of matching color chips specifically laid out for fly ashes, the standard set available for soils serves adequately, and has been used in this work.

In interpreting the results it should be remembered that the color of a fly ash is a kind of an average property of the colors of its various constituent particles, and does not imply that each and every particle has the designated color. A good analogy is that of a mixture of finely-ground salt and black pepper, which is gray even though none of the particles are gray, all being either white (salt) or black (pepper).

The caution is of significance since many of the fly ashes have unexpectedly large contents of magnetic particles which are invariably much darker than other particles. Residual carbon grains are also black or very dark and contribute to the overall color where present in appreciable amounts. On the other hand, many individual inorganic fly ash spheres when viewed under a microscope are colorless, or almost so.

Total Chemical Analysis

Procedures for chemical analysis of fly ashes are complicated because of the difficulty of getting all of the fly ash into solution. Once dissolved, more or less standard procedures like those specified by ASTM for cement analysis can be applied. In this work, after considerable experimentation, we used spectrophotometric and EDTA procedures based on Jugovic's methods for rapid cement analysis. The reference is given below.

Z. T. Jugovic, "Application of Spectrophotometric and EDTA Methods for Rapid Analysis of Cement and Raw Materials" in ASTM STP 395 "Analytical Techniques for Hydraulic Cement and Concrete, pp. 65-93 (1965).

Initial dissolution of the fly ash was by fusion with sodium hydroxide pellets at 800° C in a gold crucible. The fusion time was limited to 5 minutes to avoid loss of volatiles. The melt was then dissolved in 5.5M HCl and diluted to 250 ml. Aliquots of the resulting solution were then used for elemental analyses. The specific procedures used for each element are outlined briefly below.

(a) Silicon:

This element was determined spectrophotometrically by addition of ammonium molybdate, hydrochloric acid, and oxalic acid, and measurement of absorbance of the resulting complex at 410 nm. The method is that of ASTM C 289 for silicon in cement.

(b) Calcium and Magnesium:

These elements were determined by EDTA titration procedures. Calcium is initially determined by titration at pH 12.5 using hydroxynapthol blue; at this pH the magnesium is precipitated out as $Mg(OH)_2$ and does not interfere. A second titration is carried out at pH 10 using phthalein purple, which gives the combined total analyses of calcium and magnesium. The magnesium content is determined by difference. Hydroxylamine hydrochloride is added to reduce ferric ions to ferrous ions and triethylamine is added to complex the iron and other heavy metals to avoid interference in both titrations.

(c) Titanium:

This was determined by a spectrophotometric method involving addition of tiron, EDTA and ammonium hydroxide followed by acidification with HCl to restore the yellow complex, the absorbance of which is measured at 410 nm.

(d) Aluminum and Iron:

These elements were determined spectrophotometrically after complexing with ferron. The method involves addition of the ferron reagent followed by a 30 minute aging period, and then determination of iron at 600 nm and of the combined iron and aluminum content at 365 nm. The aluminum content is determined by difference.

(e) Sodium and Potassium:

These alkalies were determined on the atomic absorption instrument using the flame emission method specified in ASTM C 114 for analyses of alkalies in cement.

(f) Phosphorus:

This element was determined spectrophotometrically by addition of molybdic and asconoic acids, heating to boiling, cooling, and measurement

of the absorbance of the resulting complex at 725 nm.

(g) Sulfur:

Because of complications with more conventional methods, the sulfur content of these fly ashes was determined on oven-dried separate specimens using the LECO automatic analyzer system. In this analysis the sulfur is converted to SO_2 by microwave combustion in flowing oxygen; the gas stream is bubbled through a solution of starch and potassium iodate, and a colorimetric titration is automatically performed and reported by the instrument.

Analyses for all of the above elements were converted to their equivalent oxides and the combined total added. The resulting sum should equal close to 100%; the generally close approach to 100% in the results obtained for each of the fly ashes provide a good indication of the overall validity of the results.

(h) Derived Analytical Parameters:

In working with fly ashes, the value for the combined contents of SiO_2, Al_2O_3, and Fe_2O_3 is used in ASTM C 618 to define Class F and Class C fly ashes. In cementitious materials in general it is customary to combine the percentage of Na_2O with the equivalent molar percentage of K_2O (the actual K_2O percentage multiplied by a factor of 0.658) to express the sum of these two as total alkalies, expressed as equivalent % Na_2O. Both of these parameters have been calculated from the total analysis figures and are separately stated for each fly ash.

Loss-on-Ignition and Carbon Contents

As stated previously, all of the analyses cited above (except sulfur) were determined on samples that had undergone fusion at 800° C.

All residual carbon or organic matter derived from the coal but retained in the fly ash would have been removed at this temperature. It is customary in analyses of fly ash (and other materials containing organic matter) to determine the loss on ignition, i.e. the weight loss in heating from 110° C to 750° C and state this parameter separately. With fly ash this serves as an approximate indication of the carbon content of the (original) fly ash. This is usually expressed as a percentage on an oven-dry basis.

In addition to determining loss-on-ignition, we also determined the actual carbon content of each original fly ash, using a standard LECO carbon analyzer. This instrument automatically determines the carbon content by burning the carbon in an oxygen stream using microwave combustion; the carbon dioxide produced is measured by an electrical resistance comparator in the gas stream, and the result is displayed automatically.

The results for both loss-on-ignition and LECO carbon are presented separately for each fly ash and stated on an oven-dry basis.

Soluble Sulfur and Soluble Alkalies

In order to determine the content of soluble, as distinguished from total, sulfate in the fly ashes, 25 g. of fly ash was added to 250 ml of deionized water, agitated for 15 minutes, filtered without rinsing, and soluble sulfate determined by gravimetric precipitation of barium sulfate. The procedure for separating the soluble material is patterned after that prescribed for soluble alkalies in cement as given in ASTM C 114. We also determined the percentage of soluble, as distinguished from total, alkalies in each fly ash, using the same dissolution procedure. The solutions were analyzed for sodium and potassium by

the same flame photometric technique used for these elements in the complete analysis scheme. The results were expressed as percentages of soluble Na_2O, K_2O, and combined alkalies as equivalent % Na_2O. We then calculated the percentage of the total alkali content of each fly ash that was soluble.

All of these results are stated in terms of percentages based on oven dry weight, rather than on ignited weight as was used for the total

Particle Size Determinations

These were carried out by the classical Andreasen pipet method as referenced below. In this procedure a suspension of particles of 1% by

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Peter Grindrod, "Application of the Andreasen Pipet Method to the Determination of Particle Size Distribution of Portland Cement and Related Materials," in ASTM SP 473, "Fineness of Cement" pp. 45-70 (1968).

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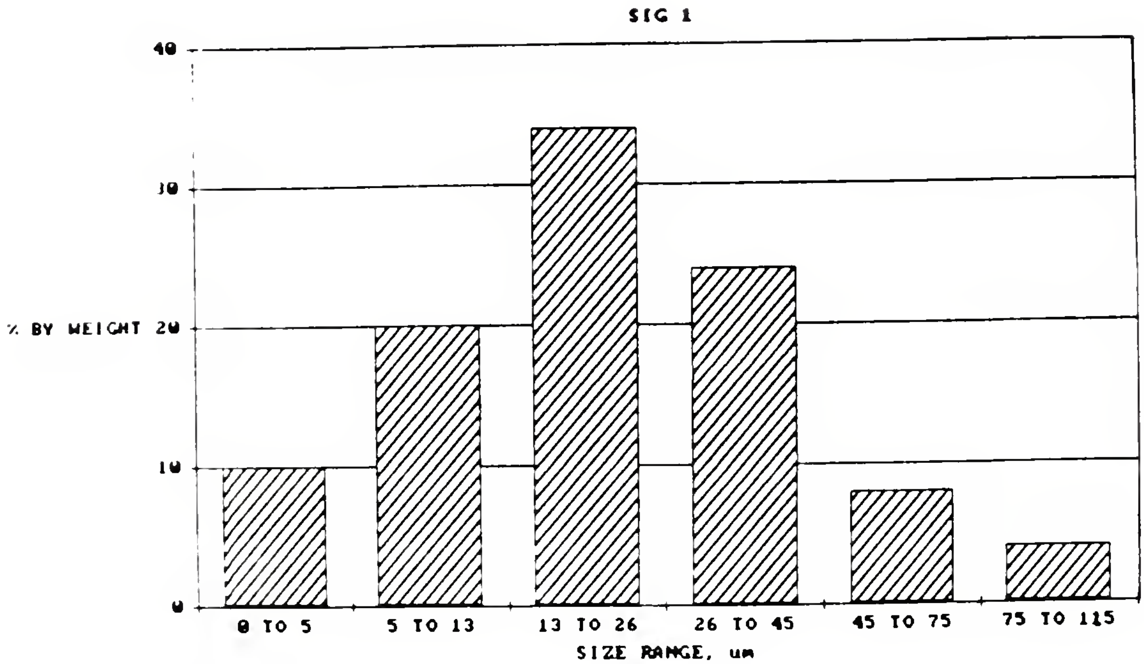
volume was dispersed in water containing 9.8 g/l of dissolved sodium hexametaphosphate dispersing agent by manual shaking, transferred to the Andreasen cylinder, and allowed to settle. Aliquots were withdrawn at designated intervals, dried, weighed, and after correction for dispersing agent weight, calculated as percentage of the specified sizes. The limiting particle size at each sampling was determined by Stoke's law. Aliquots were taken at times of up to 24 hours, to a diameter equivalent to about 1 µm, the practical limit of the determination.

The results for each fly ash were calculated as cumulative particle size distributions and plotted in that form. From these plots the mean particle diameter and the percentage of particles coarser than 45 µm (equivalent to the No. 325 sieve) were determined by inspection.

To further compare the details of the size distributions, one of the fly ashes of typical size distribution (SIG-1) was chosen as a standard for comparison, and its distribution displayed in the form of a bar plot. The bar plot of the "typical" SIG-1 fly ash is shown in the accompanying

figure.



The bar plot was designed in accordance with methods developed at Purdue University to properly portray differential pore or particle size distributions. These are derived from cumulative distributions by established methods. The feature of concern here is the selection of the boundaries of the size classes to be portrayed. The boundaries are established at equal intervals on a logarithmic scale rather than on a linear scale. The practical effect of this criterion is the requirement that each successive size interval (width of bar) be greater than the next smaller interval by a constant factor. In designing the bar interval boundaries, the factor selected here was 1.6. The actual bar width boundaries used were modified slightly from strict adherance to this criterion in order to keep the boundaries at whole numbers of μm (avoiding fractions), and to constrain one of the boundaries to be 45

μm. This is the size of the openings of the standard 325 mesh sieve used to define "oversize" particles in fly ash specifications.

Similar bar plots were made for each of the other fly ashes, and a comparison with the "typical" SIG-1 fly ash plot formed the basis for specific interpretation of the size distribution of each fly ash.

Specific Gravity Measurements

The specific gravities or densities of each of the fly ashes were determined using four different methods, all of them pycnometric techniques. All of the methods involved determining the mass of the sample by weighing on an analytical balance, and then determining the apparent solid volume of the particles in the sample. In each case this is done by measuring the amount of some fluid that was displaced by the particles in a vessel of known total volume. In two of the methods, the kerosene and mercury methods, the pycnometric fluid was liquid; the other two involved measurements in nitrogen gas and helium gas, respectively.

The method using kerosene was the procedure specified in ASTM C-188, "Standard Test Method for Density of Hydraulic Cement". This is the standard method that is specified for fly ashes as well as cements.

The mercury technique used was an offshoot of the mercury intrusion procedure that was used as one measure of the surface area of the flyashes. It is based on the principle that mercury will not voluntarily enter the spaces between and within the fly ash particles and fill up all of the space of the container. A positive pressure must be applied to cause it to do so. In this case, a pressure of 60,000 psi (414 MPa) was used, which should be sufficient to fill virtually all of the available non-solid space.

The two gas pycnometric methods were carried out in the same pycnometric apparatus, and differed only in the gas that was used. In such a device, it is necessary to obtain a direct measure of the volume of the gas surrounding the solid within the chamber of known volume. It is difficult to do this directly, and measurements are ordinarily carried out by use of a two-chamber device. The volume of gas within the sample chamber is inferred by a measurement of the pressure drop on opening the valve connecting the sample chamber with the second chamber also of accurately calibrated volume. A direct application of Boyle's Law permits calculation of the original volume of the gas in the first chamber, from which the volume of the sample can be obtained.

It was not expected that all of the methods would yield the same result; indeed, the reason for doing the measurement several different ways was to attempt to understand the differing structure of different fly ashes to the extent that these would be expected to cause variations among the several methods of measurement.

Content of Magnetic Particles

While it is well known that all fly ashes contain some magnetic particles, a quantitative measurement of the content of these is not ordinarily obtained. In part this has been due in the past to experimental difficulties, which appear to have been overcome in a procedure developed for this project.

In the procedure developed here, about 20 g. of fly ash is weighed out and placed into a beaker with 100 ml of water. A teflon-coated bar magnet is added, and the beaker placed over a magnetic stirrer and stirred for 5 minutes at moderate velocity. The stirrer is then turned

off, the magnet carefully recovered, and all magnetic particles brushed off and collected. The operation is then repeated as many times as required, until no further magnetic particles are found clinging to the magnet. The remaining suspension is then filtered, dried, and reweighed, and the weight percentage of the particles removed is calculated.

In experimental trials this procedure was found to yield essentially the same result irrespective of the size of the magnetic stirrer bar used. Reproducibility was excellent, repeat trials yielding values well within + or - 1% of magnetic particles.

The procedure will overestimate the content of magnetic particles for those fly ashes containing appreciable contents of soluble components, primarily the Class C fly ashes.

X-Ray Diffraction Analysis

X-Ray diffraction analyses were carried out using a Siemens D-500 diffractometer using copper radiation. Despite the fact that most fly ash particles are already sufficiently fine, the specimens were ground in a "shutter-box" device prior to analysis, to insure that the patterns did not reflect the suspected preferred location of glass on the outside of the solid particles. A typical x-ray diffraction pattern is shown in the accompanying figure.

Interpretation of the pattern for the presence of crystalline components is carried out by the usual methods, involving assignment of each of the peaks present to one (or sometimes more than one) of the crystalline substances which may be present. Interpretation of x-ray diffraction patterns of complex mixtures of crystalline components is difficult and requires specialized training and experience.

Consequently the patterns secured are not reproduced in this report, and only the resulting interpretation of the author is provided.

In addition to information on the crystalline components present that is derived from the peaks, the glass that is also normally present produces a very broad band of intensity that shifts the background upward over a range of 2Θ angles that reflects the kind of glass that is present. The relative intensity of this glass band can be used as a rough measure of the relative amount of glass present in the fly ash, and the angle 2Θ at which its maximum occurs provides an indication of the basic structure of the glass. Low calcium fly ashes are known to generally yield band maxima near 23° or 24° 2Θ (Cu radiation), the position of the main tridymite (SiO_2) peak. With increasing CaO content the maxima moves progressively upward in position and very high CaO fly ashes show a maximum at about 32° 2Θ (Cu radiation), which is the position of the main peak for the compound $C_{12}A_7$*.

In addition to determining the x-ray diffraction pattern of the whole fly ash, a second pattern was secured for the separated magnetic fraction. The results were ordinarily very different, the magnetic fraction being composed primarily of crystalline iron oxides of several types, with a trace of quartz presumably brought in by adhesion of non-magnetic particles to magnetic spheres. An x-ray diffraction pattern for a typical magnetic fraction of a fly ash is provided in the accompanying figure.

In many, but not all of the magnetic fractions, there was essentially no indication of a glass band detectable; apparently the particles involved are almost entirely crystalline iron oxides.

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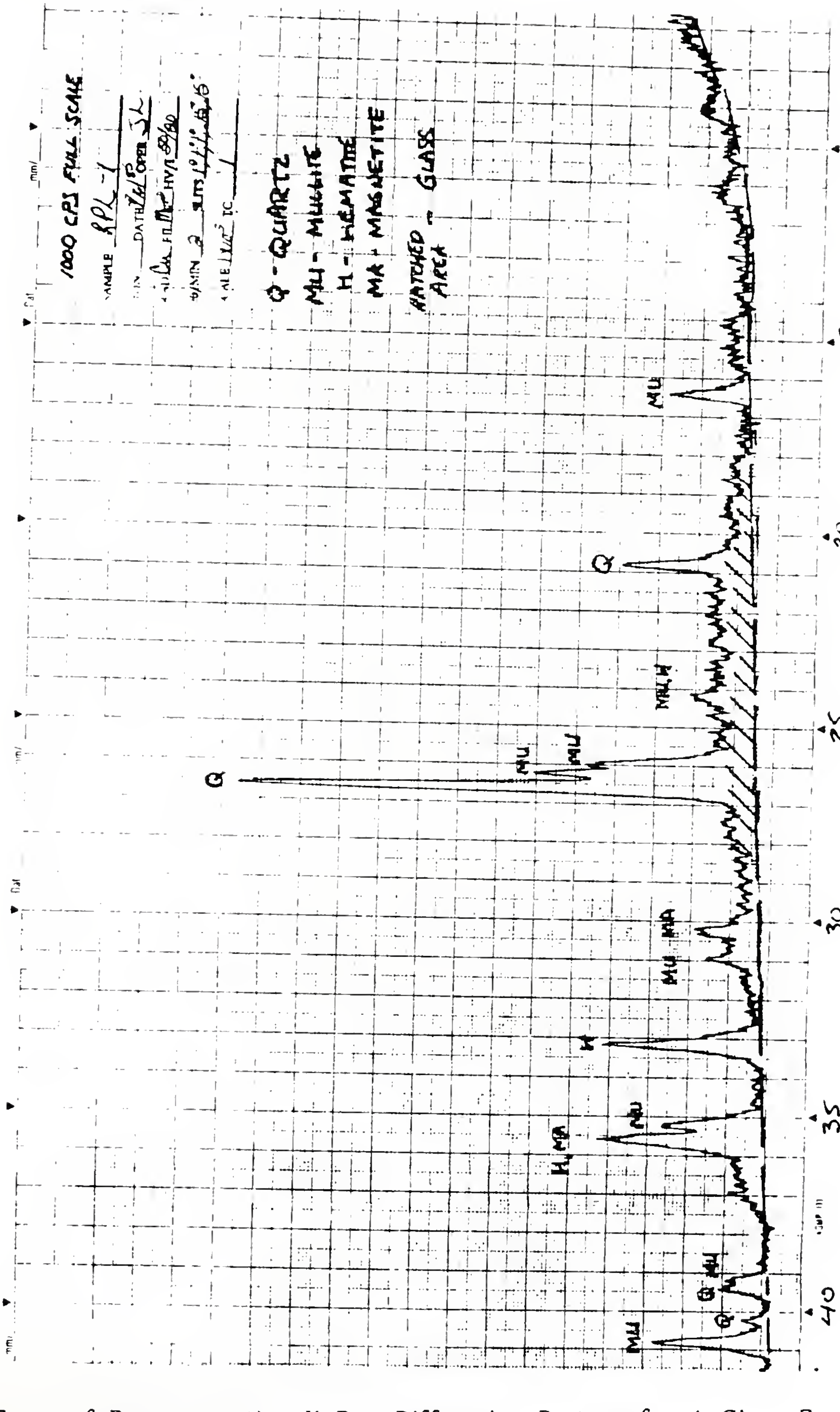
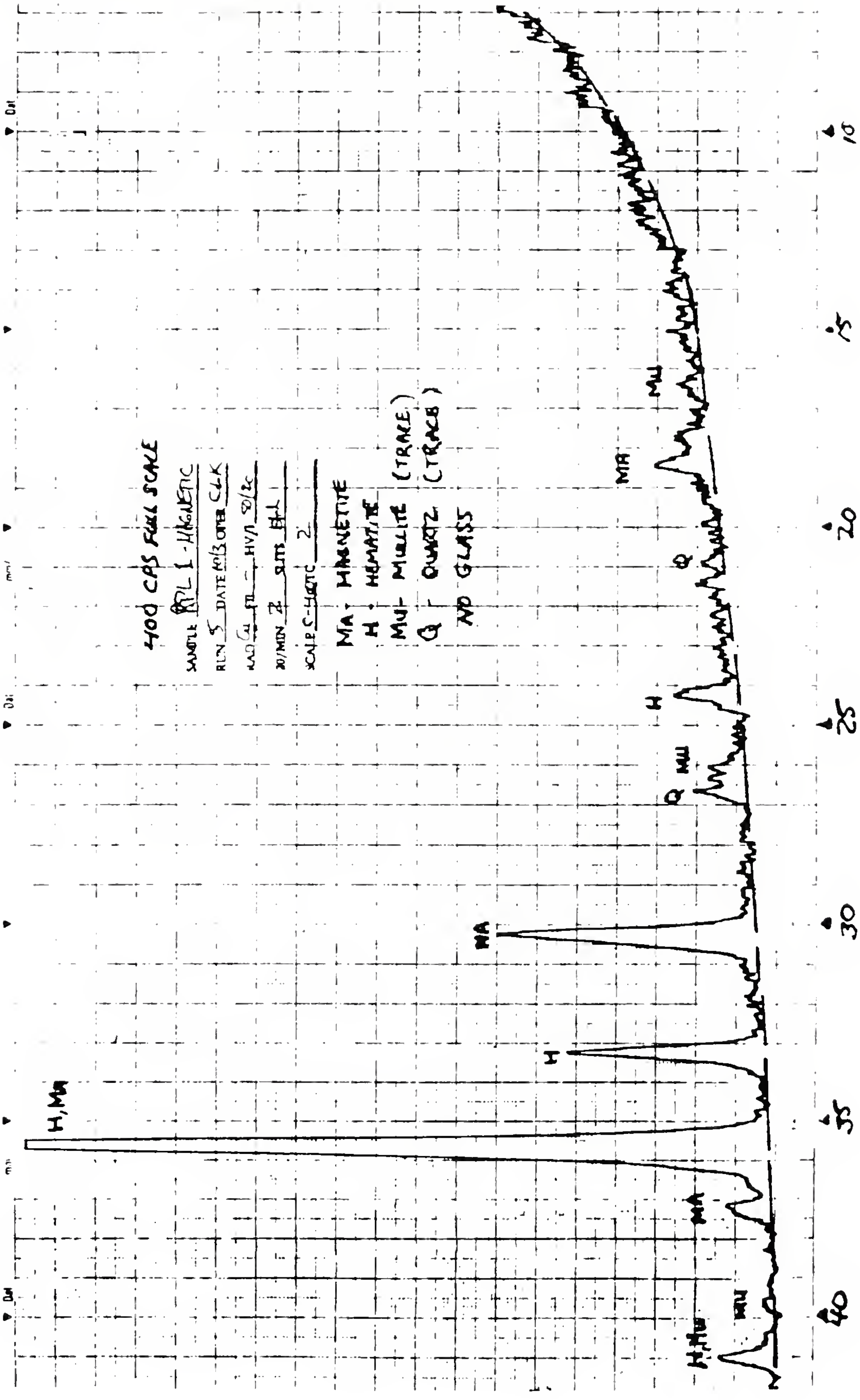
* In this work cement compounds will be described using the usual cement chemistry notation, in which C=CaO, A=Al_2O_3, S=SiO_2, etc.



Trace of Representative X-Ray Diffraction Pattern for A Class F Fly Ash (RPL-1) Showing Crystalline Peaks and Glass Band.



Trace of An X-Ray Diffraction Pattern for the Magnetic Fraction Separated from Fly Ash RPL-1, At Expanded Scale.

Scanning Electron Microscopy

Each of the fly ashes was extensively studied under the scanning electron microscope, and typically 8 to 12 micrographs of representative areas secured. A special procedure was developed for mounting fly ash specimens that overcomes much of the difficulty ordinarily found with examining fly ash in the SEM. In this procedure the specimens are mounted from acetone suspension directly on a special silver membrane filter of very fine pore structure, which provides for the retention of the spherical particles without glue, and which provides excellent conductivity and the mitigation of charging effects. The specimens are coated using an approximately 20 nm-thick coating of gold-palladium alloy, deposited in a sputter coater. The scanning electron microscope used was an ISI Super-IIIA instrument, used in the secondary electron detector mode.

The micrographs were made at magnifications permitting observation of features of a number of particles at one time, typically around 1500x to 3000x. Occasional micrographs at lower magnification were made to show wider areas or large particles, and some were made at higher magnification to image specific features on certain grains.

Of the 8 to 12 micrographs ordinarily obtained for each fly ash a set of four (or in one case six) individual micrographs was selected for inclusion in this report. The basis for selection was representativeness of the features depicted, rather than photographic excellence.

Optical Microscopy

In the original proposal for this research it was planned to

supplement the scanning electron microscope investigation of these fly ashes with study using optical microscopy. In particular, it was desired to attempt to evaluate the content of hollow particles in the fly ash, including unbroken hollow spheres, by this procedure. In addition it was felt that the glass contents of the different size ranges of spheres might be characterizable by optical microscope evaluation in crossed Nicols.

Our attempts to develop appropriate techniques for doing this were not successful.

It was originally planned to prepare mounts of fly ash particles in cyanoacrylate plastic, then grind and polish thin-sections of the resulting mounts for evaluation; the idea was that the plane of exposure would necessarily cut through many spheres and permit evaluation of whether or not they were hollow. This proved to be not possible, with the major difficulty being stripping off of the fly ash grains and of the cyanoacrylate plastic in the last stages of polishing. This resulted in considerable frustration.

Attempts to substitute epoxy for the cyanoacrylate produced another problem in that masses of tiny air bubbles were introduced into the epoxy mix. These could readily be confused with small fly ash spheres, rendering interpretation difficult. Attempts to solve the problem, and consultation with the manufacturer of the equipment being used were all fruitless.

Some attempt was made to examine individual preparations of fly ash spheres suspended in immersion oil under cover slips. While this technique was mechanically possible, the results obtained were vague, qualitative, and thought to be subject to considerable misinterpretation, especially for the smaller fly ash spheres which are

barely visible in optical microscopy. It is possible that persons more expert in optical microscopy techniques may have been able to secure more useful results from such examinations.

In any event, it is considered that the partial evaluations actually secured by this technique are not sufficiently reliable to include in this report.

Results of Pozzolanic Index Test With Cement

ASTM C 311 contains a standard test method for determination of a so-called "pozzolanic activity index with portland cement" which is considered to furnish some measure of the relative reactivity of a particular fly ash with cement. The test involves preparing and testing mortar cubes containing fly ash and reference cubes with portland cement only, aside from the standard Ottawa sand. The water content for the reference mix is adjusted to get a flow of 100 to 115. In the fly ash mortars, 30 percent of the weight of cement is replaced by an equal volume of the fly ash, calculated from the kerosene specific gravity measurement. The water content used is again that required for a flow of 100 to 115. An individual fly ash may reduce or increase the water requirement, depending on its particle size distribution and content of non-spherical particles. Both types of cubes are moist cured at 23° C in a moist room for 24 hours, then sealed and stored at 38° C for 27 days before testing. The pozzolanic activity index is the ratio of the average strength of the fly ash mortars to that of the reference cement mortars.

The test has a major weakness in that the effect of the change in water demand is confounded with the effect of the reactivity of the fly

ash. Thus a high index may result from a lowering of the water content or a high degree of reactivity, or both.

In order to provide another form of comparison of relative reactivity independent of changes in water demand, a supplementary series of tests was carried out on each fly ash. In these tests the fly ash mortars were prepared using a straight 30% weight replacement instead of one based on equal volume, and more important, the water content of the fly ash mixes was not adjusted for changes in water demand, but was left the same as that of the reference cement mortar. The result is thought to provide a more direct measure of relative reactivity of the fly ash uninfluenced by changes induced by variations in water content.

A comparison of results by the two different methods for a given fly ash provides a much more reliable interpretation of the properties of the fly ash with cement than would the results of either method by itself.

In these studies, the portland cement originally used (cement "A") produced mortars of generally low strengths. In order to see to what extent the results might have been influenced by this specific choice of cement, a partial replicate series was undertaken using a different cement (cement "B") which produced mortars of a much higher general strength level. Nevertheless, as seen in the results for those fly ashes where the comparison exists, the indexes for both types of tests with the higher strength cement "B" were practically identical to the indexes with the original cement, suggesting that the method does indeed provide results that characterize the fly ash and do not depend on the particular cement used with it.

Fly Ash No. 1: NIP-1

Unit 15, Schahfer Station, Northern Indiana Public Service Co.
Jasper County, IN (Northwest Indiana)

Introduction

This unit, part of a large dual-unit Station, burns Eastern bituminous coal and produces Class F fly ash, in contrast to its companion unit, which burns a Western lignitic coal that produces a high calcium Class C fly ash. The rated capacity of the unit is 520 MW. Sampling was done directly from a precipitator hopper.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 7/1. The verbal equivalent is "light gray" .

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	2.64
% SiO_2	59.2
% Al_2O_3	23.0
% Fe_2O_3	4.83
% Na_2O	0.55
% K_2O	0.57
% SO_3	3.13
% MgO	2.84
% P_2O_5	1.04
% TiO_2	1.10
Total	98.90

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3 .... 87.0

Total alkalies, as equivalent % Na_2O 0.93

(3) Other analyses

Loss on ignition, ignited wt. basis...........	2.24
% carbon by LECO analysis, ignited wt basis...	0.18
The following are determined on oven dry basis:	
% Total SO_3..................................	3.53
% Soluble SO_3................................	2.81
Percentage of the total SO_3 that is soluble....	80%
% Total alkalies, as equiv. % Na_2O............	0.91
% Soluble Na_2O................................	0.17
% Soluble K_2O.................................	0.12
Soluble alkalies, as equivalent % Na_2O........	0.25
Percentage of the alkalies that are soluble....	27%

(4) Chemical analysis interpretations

This is a low CaO (2.6%), low carbon (0.2%) fly ash. The SiO_2 content (59%) is unusually high. So is the SO_3 content (3.1%), essentially all of which is immediately soluble. The contents of other elements are not unusual. The alkali contents are low (0.9 as equiv. % Na_2O) and mostly insoluble.

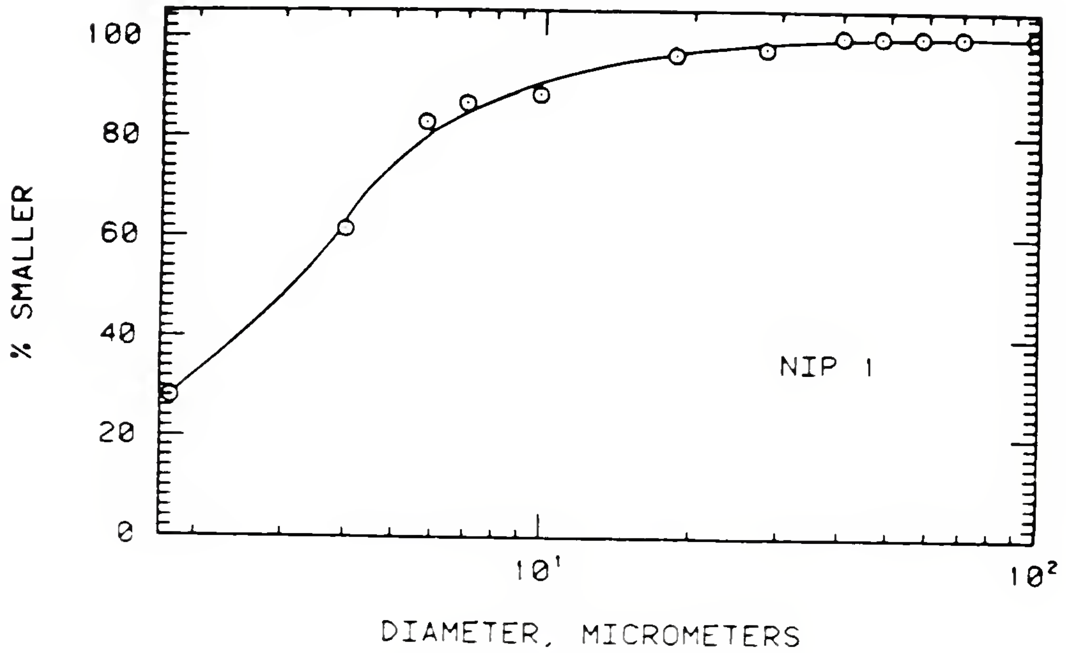
Physical Characteristics

(1) Particle size parameters

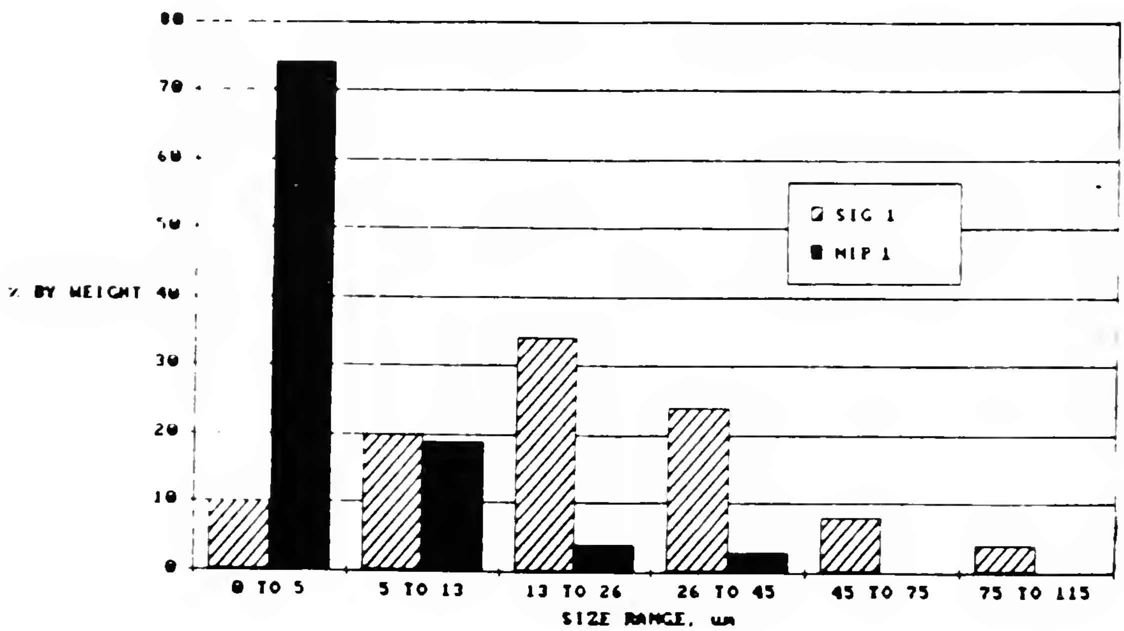
(a) Mean particle size........................ 3 µm

(b) % > No. 325 sieve (45 µm)................. 0 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Particle Size Distribution Interpretation

This is a very much finer fly ash than usual, with a weight mean particle diameter of only 3 μm, a complete absence of oversize (>45 um)

particles, and a size distribution clearly skewed to the finest particle range. This is especially evident in the comparison with the "typical" fly ash in the bar chart of the size distribution data above.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g:.................. 4.1

Surface area as measured by high pressure mercury penetration, m^2/g:................................ 4.2

Blaine fineness, cm^2/g:.......................... 7100.

Blaine fineness after ignition at 750^0C, cm^2/g..... 6500.

(b) Interpretation of surface area values:

The great fineness indicated by the particle size distribution measurements is evident from the high surface area values. The two "rigorous" methods agree as to magnitude of the true surface area (~4 m^2/g). The Blaine value is also high, and the relatively small reduction after removing the ignitable fraction confirms that little of the surface is due to carbon.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.45

Specific gravity as measured by high pressure mercury penetration.............................. 2.45

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 3.02

Specific gravity by gas displacement, using helium pycnometry............................... 2.85

(b) Interpretation

The two non-gas displacement values, based on very different physical principles, agree very well. The gas displacement methods are both significantly higher. The implication is that some spaces may be present that can be penetrated by gas but not by kerosene or mercury.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured weight content of magnetic particles of this fly ash was 15.5% after oven drying. This is a low content compared to most fly ashes, but still three times as great as the Fe_2O_3 content of about 5%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern yields peaks for a relatively low content of crystalline components, quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$).

(b) Glass: There is an unusually intense glass band in this fly ash, centering at about 23° 2Θ (Cu radiation), indicative of an unusually high content of silica (tridymite type) glass.

(c) Separated Magnetic Fraction: The small content of magnetic fraction separated from this fly ash shows no apparent glass band at all. The crystalline components appear to be a combination of magnetite (Fe_3O_4), hematite (Fe_2O_3), and maghemite (Fe_2O_3) with a small content of quartz (SiO_2) and possibly wüstite (FeO). Additionally, several large magnetic lumps have been found with the fly ash, which when x-rayed separately gave a pattern for a mixture of wüstite (FeO), magnetite (Fe_3O_4) and ε-Fe_2O_3.

Scanning Electron Micrographs

Of the micrographs taken for this particular fly ash, a set of four were chosen as representative. They are described below.

(1) Descriptions of Micrographs

NIP 1 - A. This micrograph, taken at a high magnification of 5,000x, shows a typical area of extremely fine spherical particles. There is an evident tendency for the particles to stick together to an unusual degree in fly ashes. The particles are mostly smooth, although the larger 5 μm particle in the lower right corner has a "decorated" surface. Several thin plates and tiny rods are present.

NIP 1 - B. This micrograph shows what appears to be a stuck-together cluster of very fine spheres, most less than 1 μm in diameter, with a few somewhat larger spheres also visible. Here the larger spheres appear to have clean surfaces.

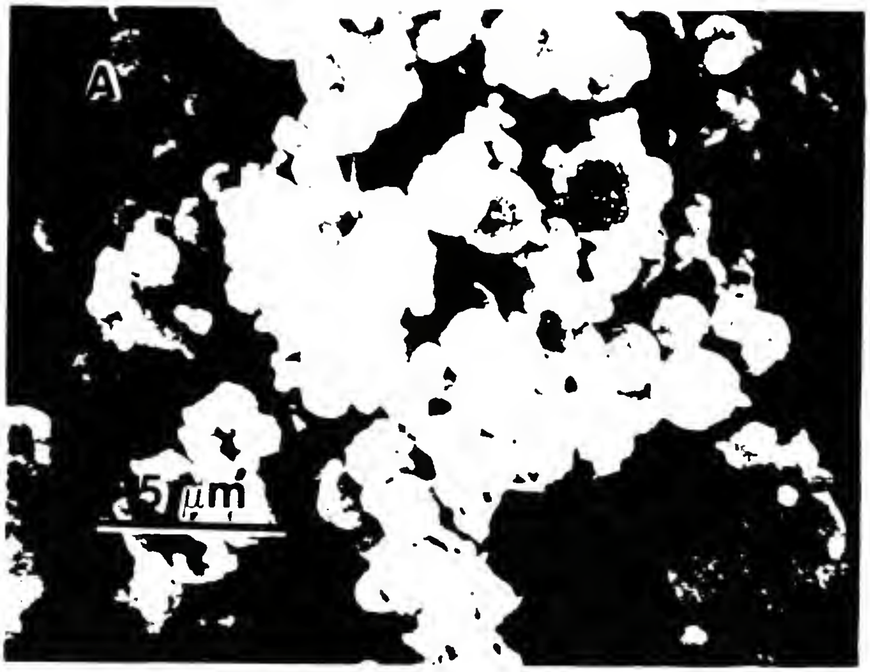
NIP 1 - C. Here a few of the larger particles are visible. This micrograph, taken at 3,000x, shows several spheres in the 5 μm range, and one large not quite spherical partly hollow grain about 10 μm in size. Again surfaces are smooth and nearly all particles are spherical.

NIP 1 - D. This final micrograph, again taken at 5,000x shows an area where most of the spheres are coarser than the majority previously shown, but below 5 μm. A few rods or thin plates can be seen as well.

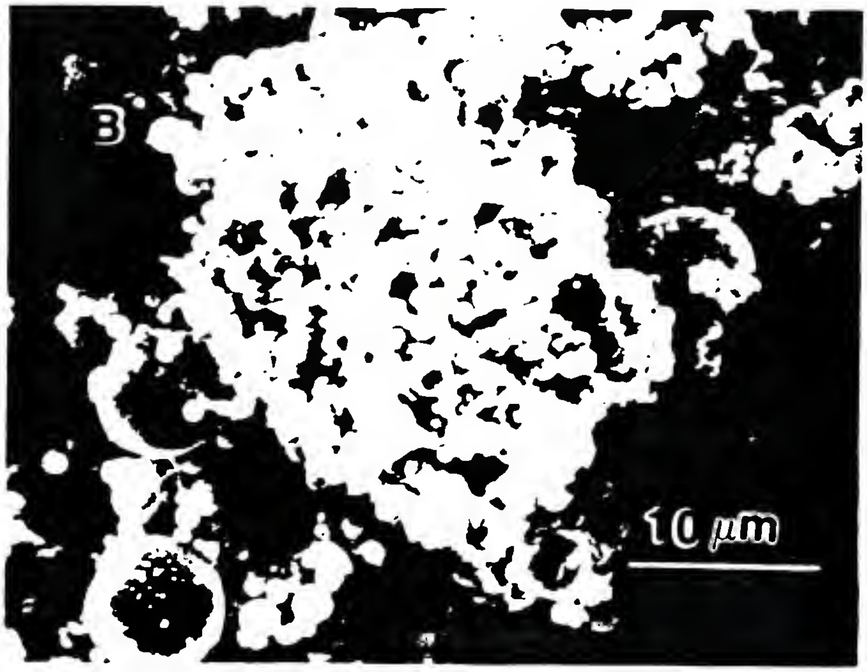
(2) Overall Interpretation

It is evident that the micrographs accord well with the expected size distribution shown in the relative particle size bar plot, where the overwhelming preponderance of particles are indicated as being below 5 um.

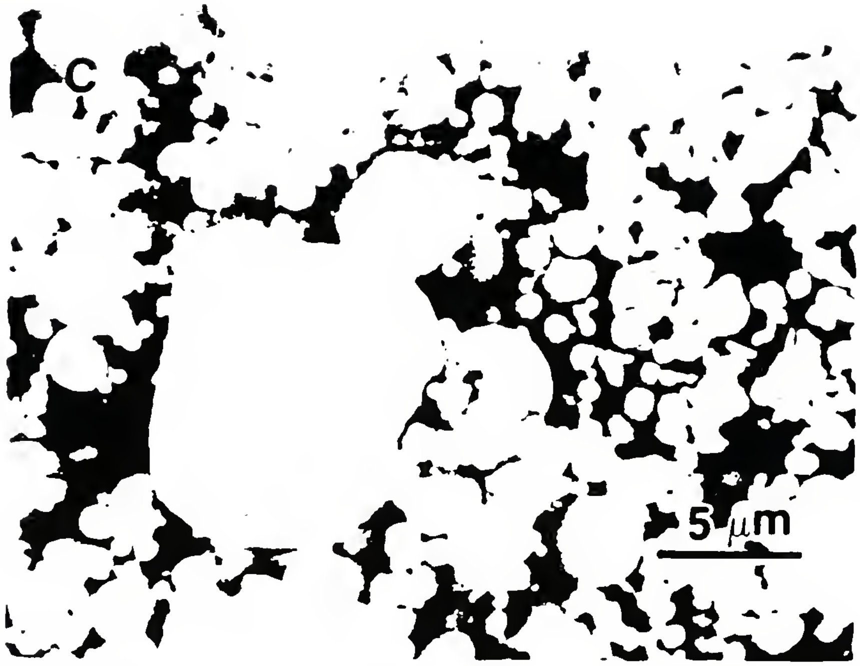
The particles are essentially all spherical, and there is no indication



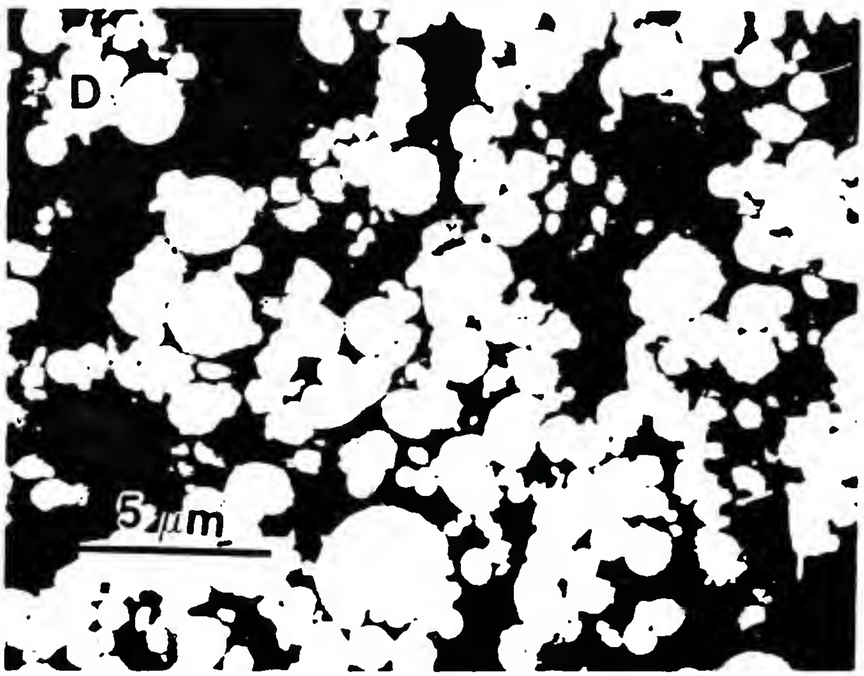
NIP 1 - A Magnification: 5000x.



NIP 1 - B Magnification: 2500x.



NIP 1 - C Magnification: 3000x.



NIP 1 - D Magnification: 5000x.

that any of the spheres are hollow.

There is a virtually complete absence of particles which might be identified as residual unburned carbon grains, according well with the LECO carbon analysis of only 0.5%.

The tiny plate and rod-shaped particles may be soluble sulfate, presumably mostly calcium sulfate in the absence of appreciable amounts of soluble alkalies recorded in the chemical analyses.

Results of Pozzolanic Index Test With Cement

Trials carried out with this fly ash using portland cement "A" gave the highest pozzolanic index recorded of any fly ash, strength being 144% of that of the reference portland cement mortar in the standard pozzolanic index test. In part this was due to substantial reduction in water demand, the water demand for the standard flow being reduced some 14%. Nevertheless it appeared that this excellent result must be at least partly due to the reactivity stemming from the fine particle size and high glass content of this fly ash.

This was confirmed on testing the fly ash at a straight 30% weight replacement for the cement, at the original water content. Here the "weight replacement pozzolanic index" was 124%, showing the high strength-producing effect of this fly ash independent of its effect on water demand.

Summary Characterization

This fly ash is an unusually fine, high surface area, low-calcium, siliceous, high glass content fly ash of very low carbon content. It has some soluble sulfate but is otherwise free of soluble components. It appears to be highly reactive with cement and has a low water demand, and should be an extremely effective admixture material in concrete.

Fly Ash No. 2: NIP-1A

Unit 14, Schahfer Station, Northern Indiana Public Service Co.
Jasper County, IN (Northwest Indiana)

Introduction

This fly ash was sampled from a companion unit identical to that of the previous one in size, but burning a Western lignite coal and so producing a much different fly ash. An analysis of the coal inorganic fraction supplied by the utility indicates a CaO content of the raw coal inorganic material of 29%. The fly ash produced from such coal is necessarily a high calcium fly ash that will be classified as an ASTM Class C material.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 5/3. The verbal equivalent is "olive".

Chemical Analyses

(1) Total analysis, ignited weight basis:

% CaO	31.0
% SiO_2	32.6
% Al_2O_3	15.2
% Fe_2O_3	10.3
% Na_2O	0.74
% K_2O	0.95
% SO_3	5.98
% MgO	3.63
% P_2O_5	1.33
% TiO_2	0.74
Total	102.5

(2) Parameters derived from above analyses:

Total % of SiO_2 + Al_2O_3 + Fe_2O_3 .... 58.1

Total alkalies, as equivalent % Na_2O 1.37

(3) Other analyses

Loss on ignition, ignited wt. basis...........	9.30
% carbon by LECO analysis, ignited wt basis...	8.33
The following are determined on an oven-dry basis:	
% Total SO_3	5.54
% Soluble SO_3..................................	0.95
Percentage of the total SO_3 that is soluble:...	17%
% Soluble Na_2O................................	0.17
% Soluble K_2O.................................	0.12
% Total alkalies, as equiv. % Na_2O............	1.25
% Soluble alkalies, as equiv. % Na_2O..........	0.25
Percentage of the alkalies that are soluble:...	20%

(4) Chemical analysis interpretations

This is a very high CaO (31%) fly ash. As in most such Class C fly ashes, the sum of the SiO_2, Al_2O_3, and Fe_2O_3 contents is much less than in typical Class F fly ashes; the sum of these oxides here being 58%. The SO_3 content (5.5%) is unusually high, but less than 20% of the sulfate is soluble. The MgO content (3.6%) is fairly low for such a high CaO content fly ash. The alkali content is fairly low (a little over 1%), but about 20% of it is soluble. An unusual feature for this fly ash is its high carbon content, well over 8%; most high calcium fly ashes tend to have low levels of unburned carbon.

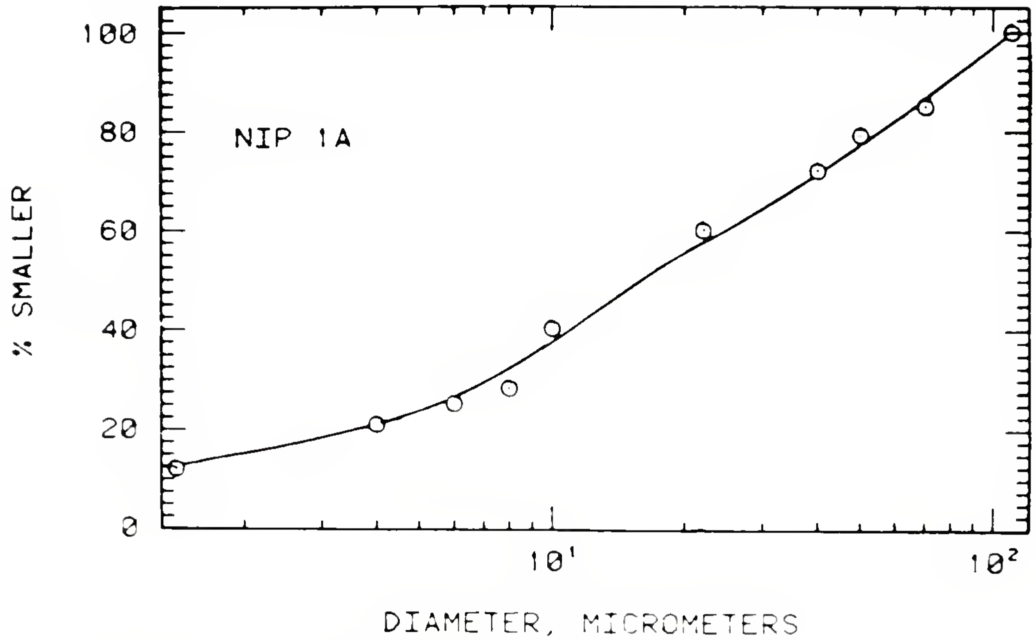
Physical Characteristics

(1) Particle size parameters

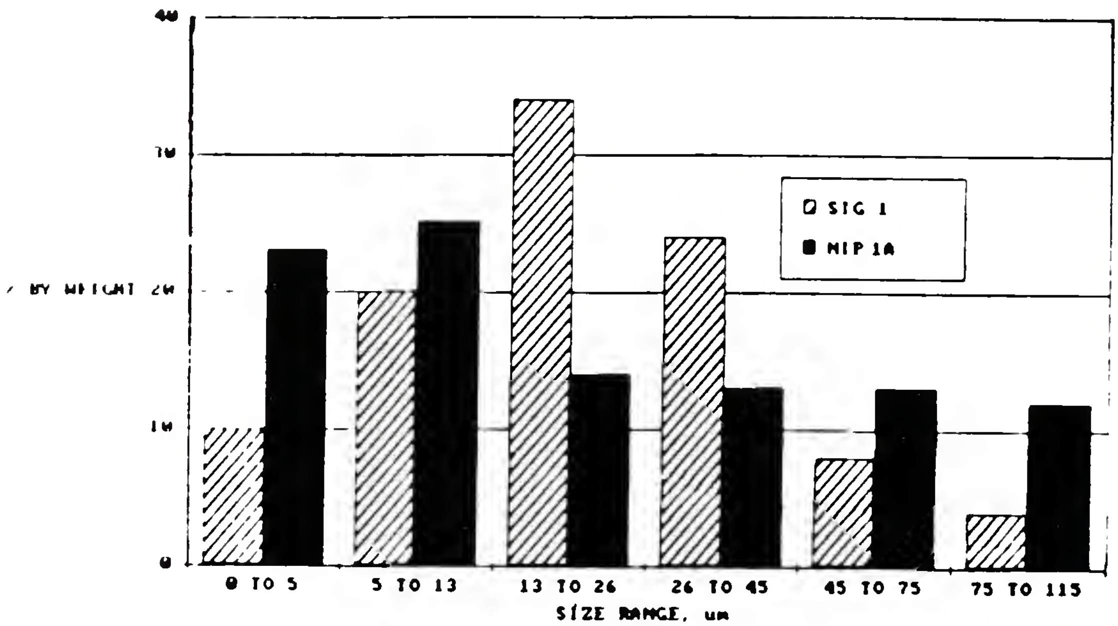
(a) Mean particle size...................... 15 µm

(b) % > No. 325 sieve (45 um)............... 25 %

(2) Particle size distribution plot



(b) Relative particle size bar plot



(4) Particle size distribution interpretation

This is a very different particle size distribution than that of the previous fly ash, although it is also an unusual one. The mean particle

diameter of 15 μm is about average for fly ashes, but the distribution has an unusual pattern. As indicated in the data above, there is a rather substantial content of oversize (> 45 μm) material, 25% to be specific. Further, as indicated in the bar chart above, half of this is very coarse, i.e. > 75 μmm. On the other hand, there is also a larger than usual proportion of very fine materal, less than 5 μm. Thus, while the mean particle size is similar to that of the "typical" Sig 1 fly ash used for comparison, the size distribution is very different and much broader.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................... 7.5

Surface area as measured by high pressure mercury penetration, m^2/g.................................. 3.8

Blaine fineness, cm^2/g:............................5200.

Blaine fineness after ignition at 750°C, cm^2/g.....2800.

(b) Interpretation of surface area values:

The water vapor surface area is extremely high for a fly ash, presumably reflecting both the high content of fine particles and the very h9igh carbon content. The mercury penetration surface area is much lower. In contrast to the previous fly ash, igniting the material to burn off the organic matter decreases the measured Blaine fineness by a factor of about two, from a high initial value of over 5000 to a more reasonable 2800 cm^2/g.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.69

Specific gravity as measured by high pressure mercury penetration.............................. 2.71

Specific gravity by gas displacement, using helium pycnometry................................ 3.00

(b) Interpretation:

As for the previous fly ash, the two non-gas displacement values, based on very different physical principles, agree very well. For this fly ash the value obtained, about 2.70, is significantly higher than the 2.45 recorded for the previous one. This is true apparently in spite of the large content of unburned carbon, which tends to reduce the density. The helium pycnometry method yielded a result that was even higher than the non-gas methods, as might be expected.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured content of magnetic particles of this fly ash was 13.1% by weight oven drying. This is a relatively low content compared to most fly ashes. It is roughly the same order of magnitude as the analytical Fe_2O_3 content (about 10%).

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The crystalline components detected in the x-ray diffraction pattern for this fly ash were anhydrite ($CaSO_4$), free

lime (CaO), tricalcium aluminate (C_3A) and/or merwinite ($Ca_3Mg(SiO_4)_2$), periclase (MgO), and only a trace of quartz (SiO_2). This is a fairly common assemblage for a high-calcium Class C fly ash derived from lignitic Western coal.

(b) Glass: The glass band or "background hump" indicated the presence of a reasonably high content of the calcium aluminate type glass, with a maximum position of about 32° 2Θ (Cu radiation).

(c) Separated magnetic fraction: The x-ray pattern of the magnetic material indicated the presence of maghemite (Fe_2O_3), magnetite (Fe_3O_4), hematite (Fe_2O_3), a recognizable content of gehlenite (C_2A_2S), and a trace of quartz. There was some indication of a weak glass band at high 2Θ angles, centered around 33°.

Scanning Electron Micrographs

A set of four of the micrographs taken from samples of this fly ash were chosen as representative. They are described below.

(1) Description of micrographs

NIP 1A - A. This micrograph, taken at a very low magnification of only 100x, shows the great disparity in sizes of the individual fly ash particles in this material. There are five grains well over 100 µm in size; two of them are clean spheres, one is a sphere with a deposit on it, and two are irregular complex grains (visible in the upper left part of the figure. These contrast strongly with the thousands of very much smaller spheres present in the whole area depicted.

NIP 1A - B. The appearance of one of these complex grains at higher magnification is shown in this micrograph. It is a complex of layered unburned coal structure with pockets containing hundreds of tiny fly ash

spheres, each typically 1 or 2 µm in diameter. The spheres would have been liberated had the carbon in this particular ground coal fragment burned up. Since it has remained as a residual ground coal fragment, the spheres are mostly still associated with it except for a few that have shaken loose.

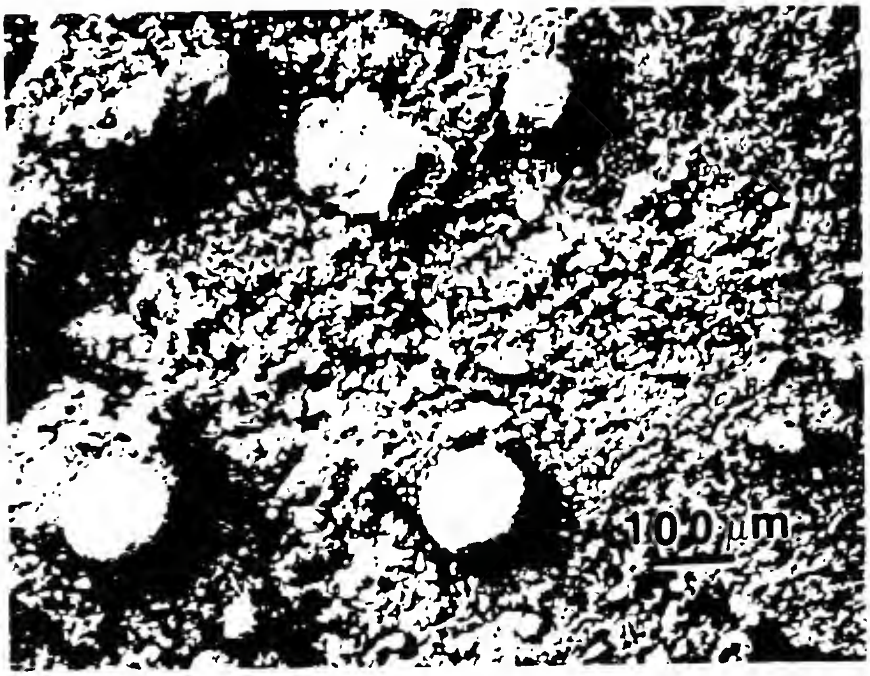
NIP 1A - C. Here at still higher magnification (5,000x) is the appearance of typical free fly ash spheres of this material. It is evident that the surfaces are not smooth, but are either heavily coated with a deposit of some kind or are intrinsically rough-textured. Note that there is a fair content of tiny spheres, going down to below 1 µm in size.

NIP 1A - D. This final micrograph, again taken at 5,000x shows an area where the fly ash particles are individually free spheres, but they are locally accompanied by fragments and pieces of unburned coal. This is a very typical area for this particular fly ash, nearly all fields showing both many spheres and appreciable numbers of carbon residue fragments.

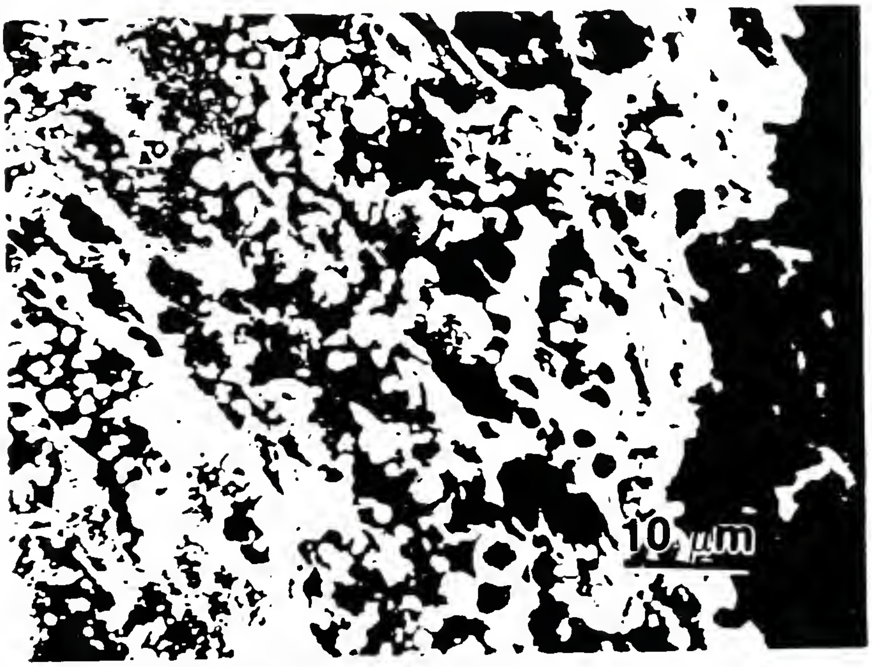
(2) Overall Interpretation

Again the scanning electron micrographic representation is in accord with the particle size distribution data, and graphically illustrates the extremes of particle size present.

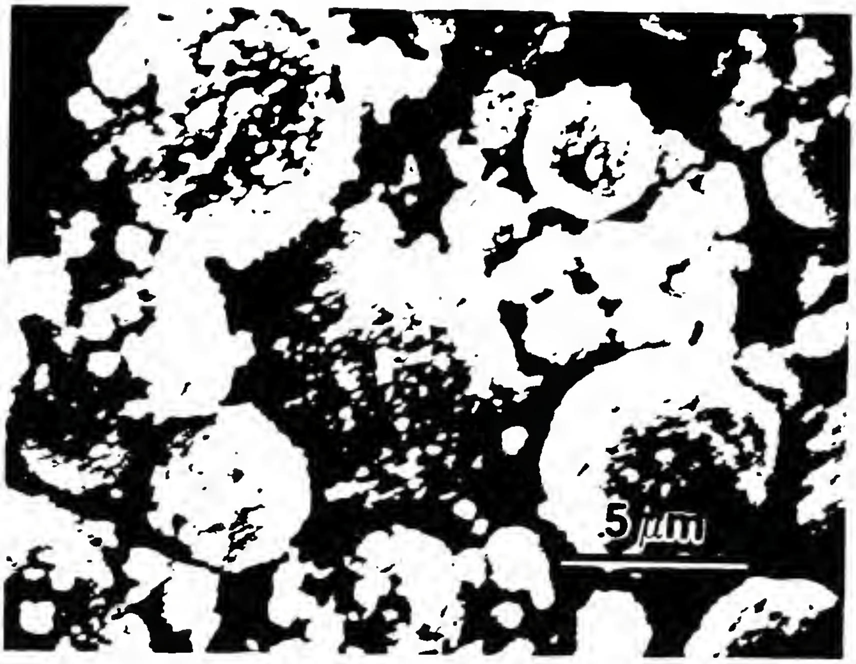
The large content of unburned carbon fragments would be expected in view of the high carbon content of this material. The very rough character of the individual fly ash spheres is also no surprise; previous experience has shown that many Class C fly ashes tend to have such a rough surface character. Sometimes the rough surface can be interpreted as a deposit of soluble material, usually sulfates, from the boiler atmosphere after the fly ash has reached a cooler zone and the spheres have been formed;



NIP 1A - A Magnification: 100x.



NIP 1A - B Magnification: 1500x.



NIP 1A - C Magnification: 5000x.

NIP 1A - D Magnification: 5000x.

however, that is not so in the present case, in view of the limited amount of soluble material shown on tests.

No evidence of cenospheres or other hollow grains was detected, and in view of the relatively high specific gravity values recorded, the content of such particles should be very small.

The unusual size distribution of this fly ash may be the result of a malfunctioning economizer unit, which ordinarily serves to remove most of the very coarse particles before the gas stream bearing the fly ash reaches the electrostatic precipitator where the fly ash is collected.

Results of Pozzolanic Index Test With Cement

Trials carried out with this fly ash using portland cement "A" gave a poor result in the standard pozzolanic index, the strength recorded being only 51% of the control mortar. However, a test carried out at a straight 30% weight replacement level with no adjustment in water content gave a "weight replacement pozzolanic index" value of 81%, a fully acceptable value. The difference was apparently not due to excessive water demand, since the incorporation of the fly ash actually reduced the water requirement for the specified flow slightly.

Summary Characterization

This fly ash is a high-calcium fly ash of reasonably typical chemistry, with moderate sulfate and modest alkali contents. It has the usual reactive crystalline components characteristic of high-calcium Class C fly ashes, and the calcium aluminate-type glass structure. It undoubtedly would be a good fly ash except for its high content of oversized material and its very high carbon content. The latter factor, and perhaps the former as well

are due to plant operational characteristics that might be improved in the future.

Fly Ash No. 3: NIP-2

D. H. Mitchell Station, Northern Indiana Public Service Co.
Lake County, IN (Northwest Indiana)

Introduction

This fly ash was sampled from a common silo serving 4 separate boilers at this plant, which is a medium-sized facility totalling 505 MW in capacity. Two different coals, both Western lignitic coals, were being burned in this facility. Two of the four units were operating under base load burning conditions, the other two in mostly peak load operation. The fly ash was being marketed through an independent broker.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 10YR 6/3. The verbal equivalent is "pale brown".

Chemical Analyses

(1) Total analysis, ignited weight basis:

% CaO	35.2
% SiO_2	25.3
% Al_2O_3	12.7
% Fe_2O_3	9.1
% Na_2O	0.58
% K_2O	.60
% SO_3	3.83
% MgO	10.9
% P_2O_5	0.66
% TiO_2	0.88
Total	99.8

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3............... 47.1

Total alkaliet, as equivalent % Na_2O........... 0.98

(3) Other analyses

Loss on ignition, ignited wt. basis...........	0.50
% carbon by LECO analysis, ignited wt basis...	0.14
The following are determined on an oven-dry basis:	
% Total SO_3	3.86
% Soluble SO_3..............................	0.52
Percentage of the total SO_3 that is soluble....	13%
% Soluble Na_2O..............................	0.14
% Soluble K_2O..............................	0.02
% Total alkalies, as equiv. % Na_2O............	0.98
% Soluble alkalies, as equiv. % Na_2O..........	0.15
Percentage of the alkalies that are soluble....	15%

(4) Chemical analysis interpretations

This is clearly one of the very high CaO content variety of Class C fly ash, with an extraordinary 35% CaO content. This limits the combined SiO_2 + Al_2O_3 + Fe_2O_3 content to just under 50%. At just under 4%, the sulfate content is high, although not as high as that of the previous fly ash. The alkali content is modest (about 1%), and almost none of it is soluble. There is an extremely high MgO content, over 10%, in this sample. Operation of the power plant boiler appears to be extremely efficient, the residual carbon content being only about 0.1%; this is the lowest value of all fly ashes tested in this program.

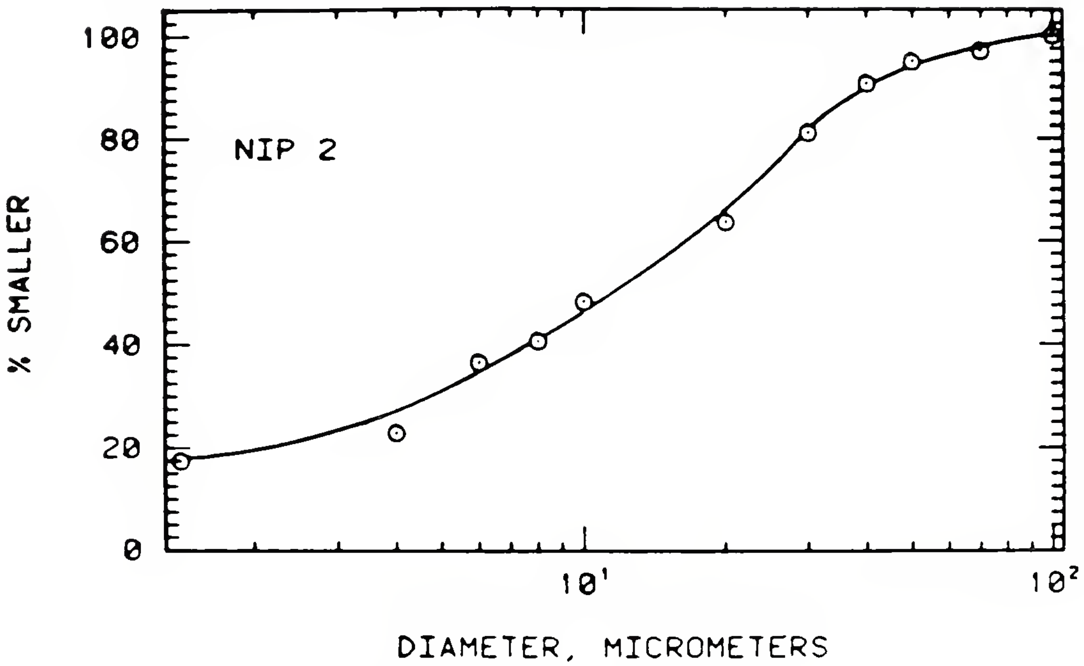
Physical Characteristics

(1) Particle size parameters

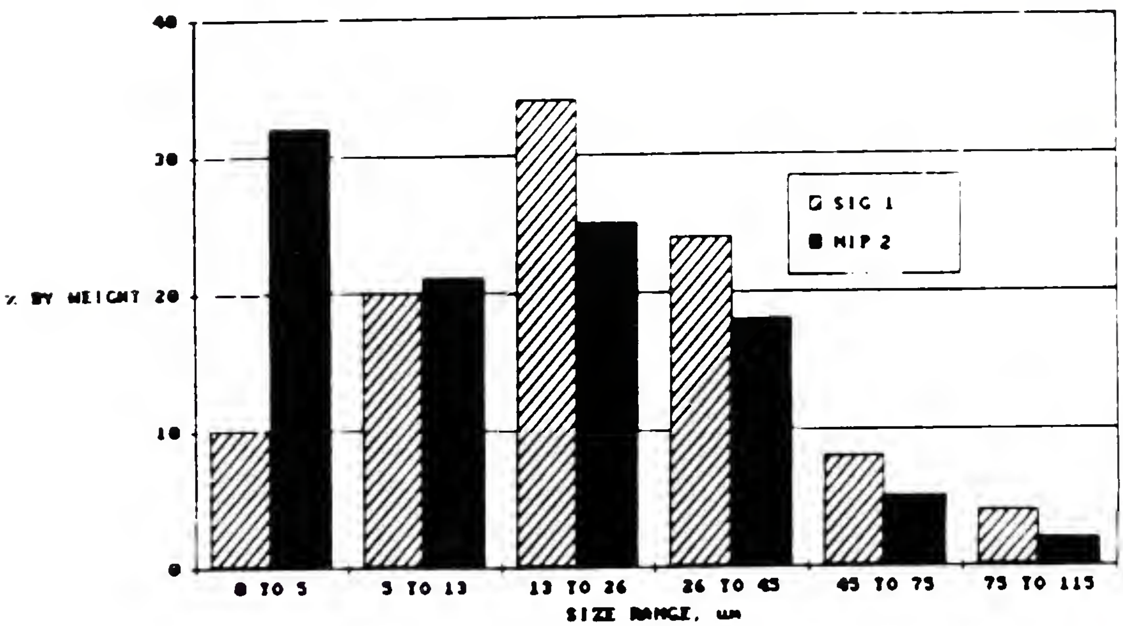
(a) Mean particle size: .... 11 µm

(b) % > No. 325 sieve (45 µm)................. 7 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Particle size distribution interpretation

This is a relatively fine fly ash, as indicated by the relatively small mean particle size (11 μm) and the small content of oversize material, only

7% > 45 µm. Examination of the bar chart shows that the general distribution of sizes is more or less similar to that of the "typical" SIG 1 fly ash except that the content of finest sizes, less than 5 µm, is more than three times as great.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................... 2.1

Surface area as measured by high pressure mercury penetration, m^2/g:.................................... 2.3

Blaine fineness, cm^2/g:........................... 3200.

Blaine fineness after ignition at 750^0C, cm^2/g...... 3500.

(b) Interpretation of surface area values:

Despite the fine particle size distribution, both the water vapor surface area and the mercury penetration surface area measured for this fly ash are not particularly high, both being close to 2.2 m^2/g. Neither is the Blaine fineness exceptionally high, only around 3200.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.81

Specific gravity as measured by high pressure mercury penetration.............................. 2.68

Specific gravity by gas displacement, using nitrogen gas pycnometry......................... 2.76

Specific gravity by gas displacement, using helium pycnometry.............................. 3.05

(b) Interpretation:

The agreement betweeen the results of the various specific gravity measurements for this fly ash is adequate, but not particularly good. The two non-gas methods average about 2.75, in agreement with the nitrogen gas pycnometry result. The helium pycnometry result is somewhat greater, as is usually the case. The values generally are high, especially for a relatively low iron content fly ash, and suggest that the particles are almost entirely solid.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured weight content of magnetic particles of this fly ash was 9.4% , which is essentially identical to its analytical content of Fe_2O_3. This is one of the lowest contents of magnetic particles of any of the fly ashes examined in this program. Very high CaO fly ashes typically do not have high iron contents and would be expected to be low in amount of magnetic fraction, although the converse is not necessarily true.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The crystalline components detected in this fly ash include free lime (CaO), quartz (SiO_2), periclase (MgO), anhydrite ($CaSO_4$), magnetite (Fe_3O_4) and hematite (Fe_2O_3).

(b) Glass component: A fairly strong glass band of the calcium aluminate structure type was present in the pattern, with a maximum at about 32° 2Θ (Cu radiation).

(c) Separated magnetic fraction: X-Ray diffraction of the magnetic fraction indicated the presence of magnetite (Fe_3O_4), hematite (Fe_2O_3),

maghemite (Fe_2O_3), and small quantities of quartz (SiO_2) and anhydrite ($CaSO_4$). There is almost no indication of any glass band.

Scanning Electron Micrographs

Of the micrographs taken for this particular fly ash, a set of four chosen as being representative are described below.

(1) Description of micrographs

NIP 2 - A. This micrograph shows an area of more or less typical spherical fly ash particles, most of them in the relatively fine size range. The surfaces of the spheres are sparsely decorated with rough projections or deposits.

NIP 2 - B. A somewhat similar area , except that some of the fly ash spheres here are a bit bigger (although still around the average size or less). The surface texture is rough, as it is in all of the micrographs of this fly ash.

NIP 2 - C This micrograph shows one of the larger grains, an incompletely spherical partly hollow particle about 80 μm in diameter. The other, smaller spheres in the area are similar to those previously shown.

NIP 2 - D This final micrograph shows a fairly unusual feature. This appears to be the remanant of a large ground coal fragment. Despite the fact that most of the carbon has been burned away, the cluster has held together, and the outline of the original fragment is still distinguishable.

(2) Overall Interpretation

The scanning electron micrographs indicate that this fly ash consists primarily of apparently solid spheres; a few large particles do occur, but

maghemite (Fe_2O_3), and small quantities of quartz (SiO_2) and anhydrite ($CaSO_4$). There is almost no indication of any glass band.

Scanning Electron Micrographs

Of the micrographs taken for this particular fly ash, a set of four chosen as being representative are described below.

(1) Description of micrographs

NIP 2 - A. This micrograph shows an area of more or less typical spherical fly ash particles, most of them in the relatively fine size range. The surfaces of the spheres are sparsely decorated with rough projections or deposits.

NIP 2 - B. A somewhat similar area , except that some of the fly ash spheres here are a bit bigger (although still around the average size or less). The surface texture is rough, as it is in all of the micrographs of this fly ash.

NIP 2 - C This micrograph shows one of the larger grains, an incompletely spherical partly hollow particle about 80 μm in diameter. The other, smaller spheres in the area are similar to those previously shown.

NIP 2 - D This final micrograph shows a fairly unusual feature. This appears to be the remanant of a large ground coal fragment. Despite the fact that most of the carbon has been burned away, the cluster has held together, and the outline of the original fragment is still distinguishable.

(2) Overall Interpretation

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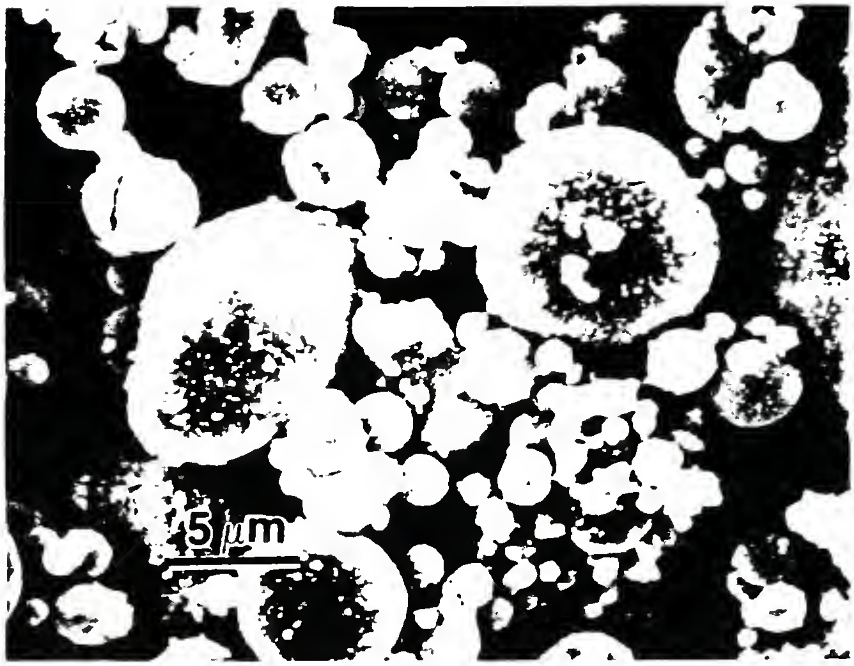
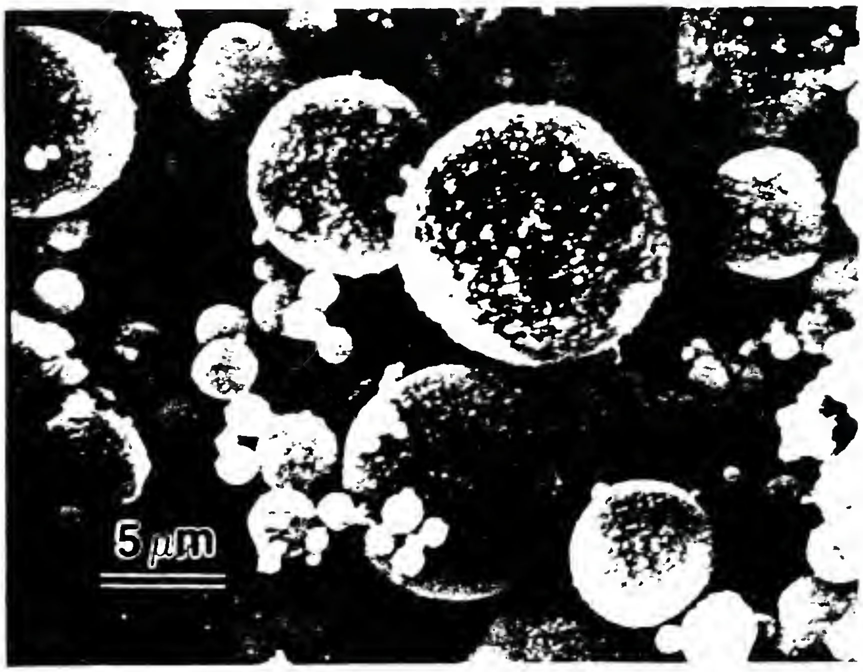
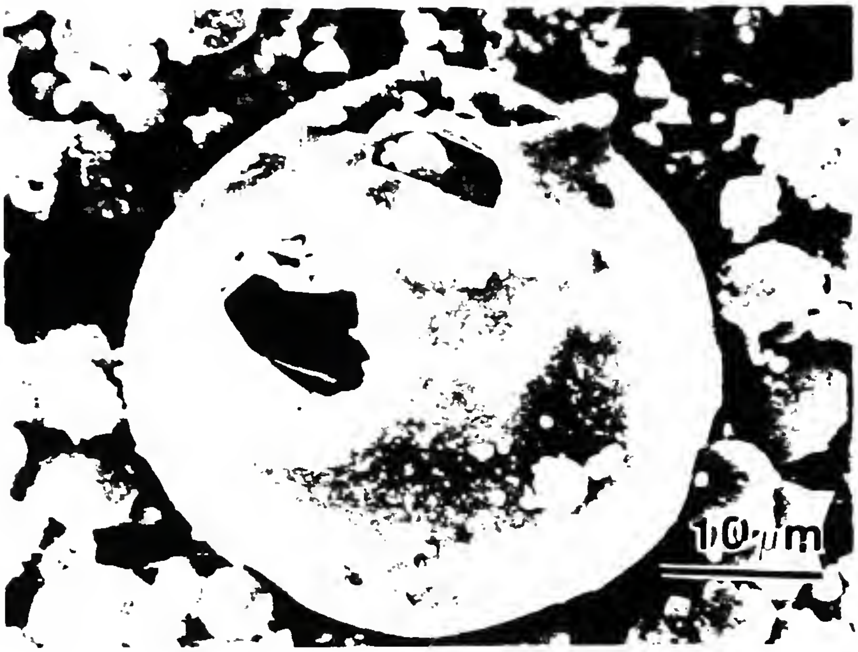


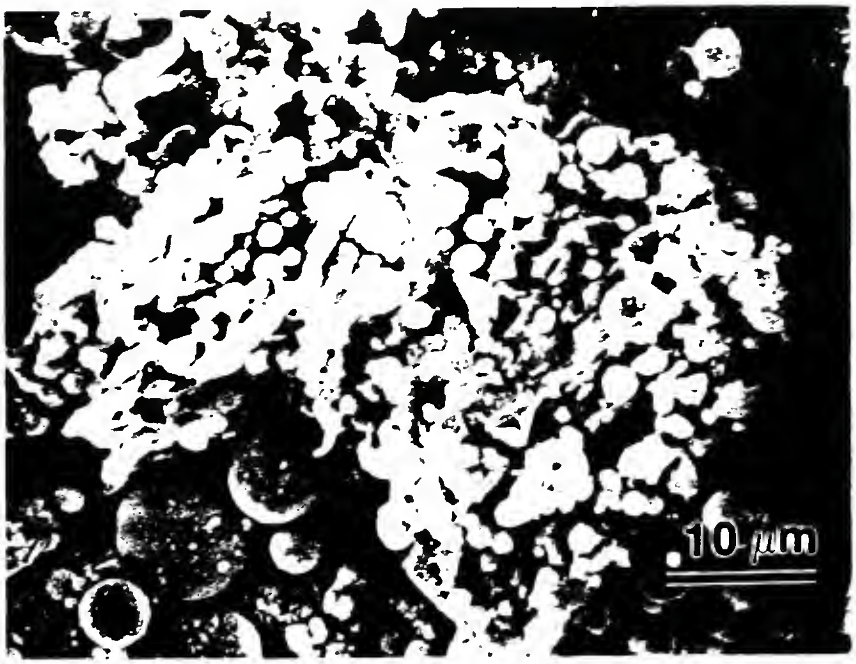
NIP 2 - A Magnification: 3000x.



NIP 2 - B Magnification: 3000x.



NIP 2 - C Magnification: 2000x.



NIP 2 - D Magnification: 2000x.

they are relatively unusual. There is virtually no indication of coal residue particles, consistent with the low indicated carbon content.

Results of Pozzolanic Index Test With Cement

The pozzolanic index test results with this fly ash were quite favorable. The standard test, carried out with portland cement "A" gave a pozzolanic index of 90%. The same type of testing with portland cement "B" yielded an almost identical value of 92.5%.

Modified tests carried out on a straight 30% weight replacement basis without adjustment of water content yielded 83% for Cement "A", and an actually identical 83% using Cement "B".

These results indicate the generally high reactivity of this quite typical high calcium Class C fly ash.

Summary Characterization

This fly ash is a relatively fine very high calcium Class C ash with the usual content of crystalline reactive calcium compounds, a moderate sulfate content, and a modest alkali content. The residual carbon is extremely low, and nearly all of the particles are solid spheres; only a small percentage of the material is magnetic. The fly ash appears to be highly reactive and yields satisfactory pozzolanic index figures. The high content of MgO (over 10%) is the only disturbing feature.

Fly Ash No. 4: IPL-1

E. W. Stout Generating Station, Indianapolis Power and Light Co.
Marion County, IN (Central Indiana)

Introduction

This fly ash was sampled from a silo serving No. 70 boiler, a 450 MW unit which is said to operate mostly in a base load mode. The coal burned is a mixture of several Illinois Basin (Eastern) coals which have been burned for many years. The ash was marketed commercially at the time of sampling as an ASTM Class F fly ash.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 5/2. The verbal equivalent is "olive gray".

Chemical Analyses

(1) Total analysis, ignited weight basis:

% CaO	1.72
% SiO_2	42.9
% Al_2O_3	26.1
% Fe_2O_3	21.1
% Na_2O	0.27
% K_2O	2.60
% SO_3	1.00
% MgO	5.23
% P_2O_5	0.66
% TiO_2	0.66
Total	102.2

(2) Parameters derived from above analyses

Total % of $SiO_2 + Al_2O_3 + Fe_2O_3$.............. 90.1

Total alkalies, as equivalent % Na_2O........... 1.98

(3) Other analyses

Loss on ignition, ignited wt. basis	1.40
% carbon by LECO analysis, ignited wt basis	1.10

The following are determined on an oven-dry basis:

% Total SO_3	1.00
% Soluble SO_3	0.42
Percentage of the total SO_3 that is soluble:	42%
% Soluble Na_2O	0.05
% Soluble K_2O	0.02
% Total alkalies, as equiv. % Na_2O	1.95
% Soluble alkalies, as equiv. % Na_2O	0.06
Percentage of the alkalies that are soluble:	3%

(4) Chemical analysis interpretations

This is a "classic" bituminous coal derived fly ash, with the combined SiO_2 + Al_2O_3 + Fe_2O_3 content over 90%. The sulfate content is small, although about half of it is immediately soluble. The alkali content, primarily K_2O, is substantial at nearly 2%, but very little of it is soluble. The MgO content is high. There is very little residual carbon, roughly 1%, indicative of excellent combustion in the boiler.

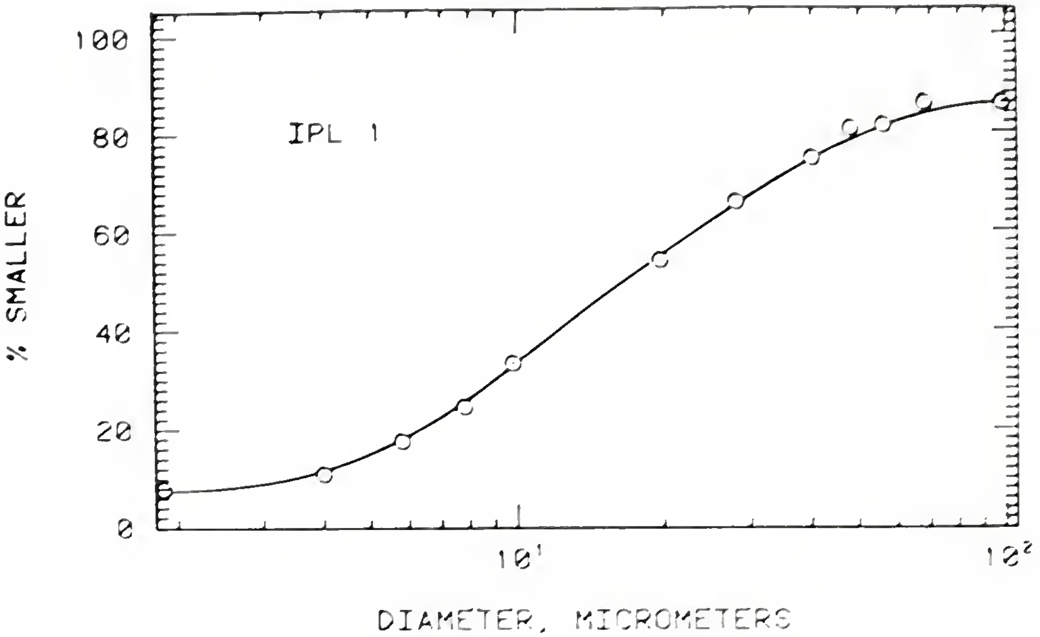
Physical Characteristics

(1) Particle size parameters

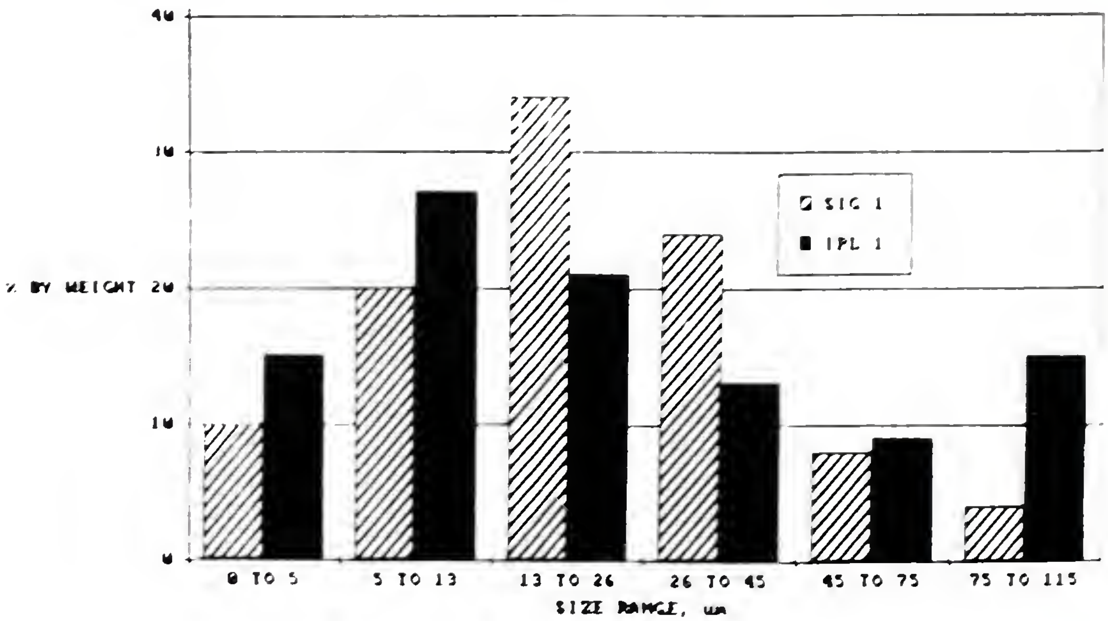
(a) Mean particle size........................ 17 µm

(b) % > No. 325 sieve (45 µm)................ 24 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Particle size distribution interpretation

This is a fairly ordinary particle size distribution, and is quite similar to that of the "typical" SIG-1 as used as the reference on the bar

chart. The mean size, 17 µm, is almost the same, but the IPL-1 fly ash has at the same time (a) a slightly greater content of fine size particles, and equally important, (b) a much greater content of very coarse sized materials, i.e. those over 75 µm. The total percentage coarser than 45 µm is a rather high 24%.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g:................... 3.8

Surface area as measured by high pressure mercury penetration, m^2/g.................................... 6.0

Blaine fineness, cm^2/g:..........................2200.

Blaine fineness after ignition at 750°C, cm^2/g......2200.

(b) Interpretation of surface area values

The water vapor surface area is about average for this fly ash, but the mercury penetration surface area is almost twice as high. The Blaine fineness is somewhat lower than average, at 2200. As expected from the very low carbon content, there is almost no change in measured Blaine fineness. after ignition.

(6) Specifc Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.50

Specific gravity as measured by high pressure mercury penetration............................. 2.59

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.52

Specific gravity by gas displacement, using helium pycnometry.............................. 2.63

(b) Interpretation:

Agreement is excellent between the results of all of the various specific gravity measurements for this fly ash, the overall average being about 2.56.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured weight content of magnetic particles of this fly ash was 43.3%. This is an extremely high content of such particles and is about twice the Fe_2O_3 content determined by chemical analysis, suggesting that a considerable part of the magnetic fraction contains other chemical components besides iron.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The crystalline components detected in the x-ray diffraction pattern for this fly ash included quartz (SiO_2), maghemite (Fe_2O_3), and small amounts of mullite ($3Al_2O_3 \cdot 2SiO_2$), magnetite (Fe_3O_4), and possibly gehlenite (C_2A_2S).

(b) Glass: A substantial glass band was present in the pattern, with its maximum at approximately 24° 2Θ (Cu radiation), indicative of the silica (tridymite-type) glass structure.

(c) Separated magnetic fraction: The x-ray diffraction pattern for the separated magnetic fraction showed strong and well crystallized peaks indicating the presence of magnetite (Fe_3O_4), hematite (Fe_2O_3), maghemite (Fe_2O_3), and a trace of quartz (SiO_2). There was essentially no indication of any glass band in the x-ray pattern.

Scanning Electron Micrographs

Of the micrographs taken for this particular fly ash, a set of four were chosen as representative and are described below.

(1) Descriptions of Micrographs

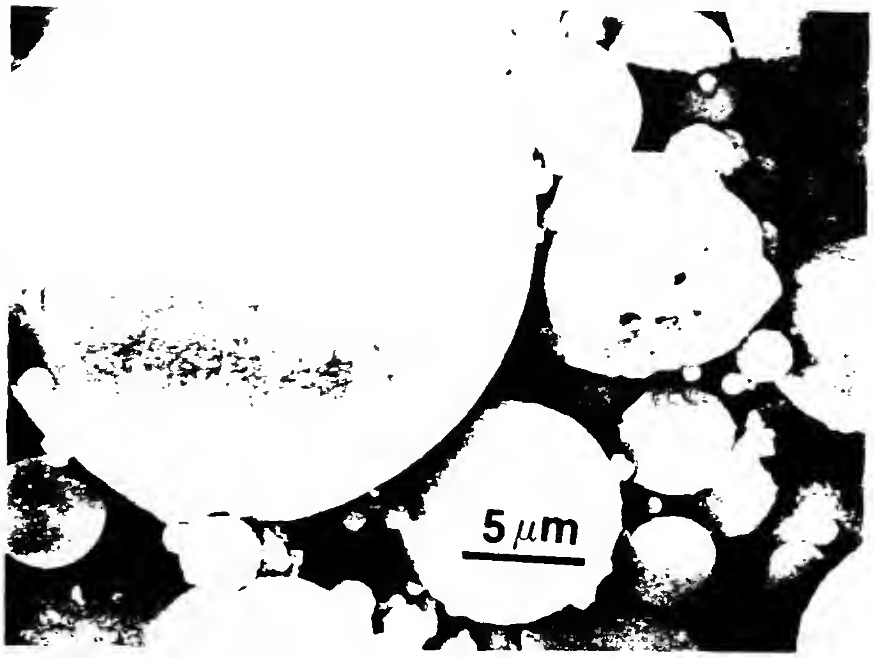
IPL 1 - A. This micrograph shows a representative collection of medium sized to finer fly ash particles. Most are spherical, but several larger particles that were incompletely melted are apparent in the lower part of the figure, and a large sphere with a smaller hemispherical bulge popping out the side is visible in the upper left portion.

IPL 1 - B. This micrograph, taken at somewhat higher magnification, again shows an area of medium-sized, mostly spherical particles. In neither this nor the preceding micrograph is there any indication of unburned carbon residue. All grains depicted are spherical except for an incompletely melted 10 μm particle in the upper right portion, which seems to have a few hollow chambers.

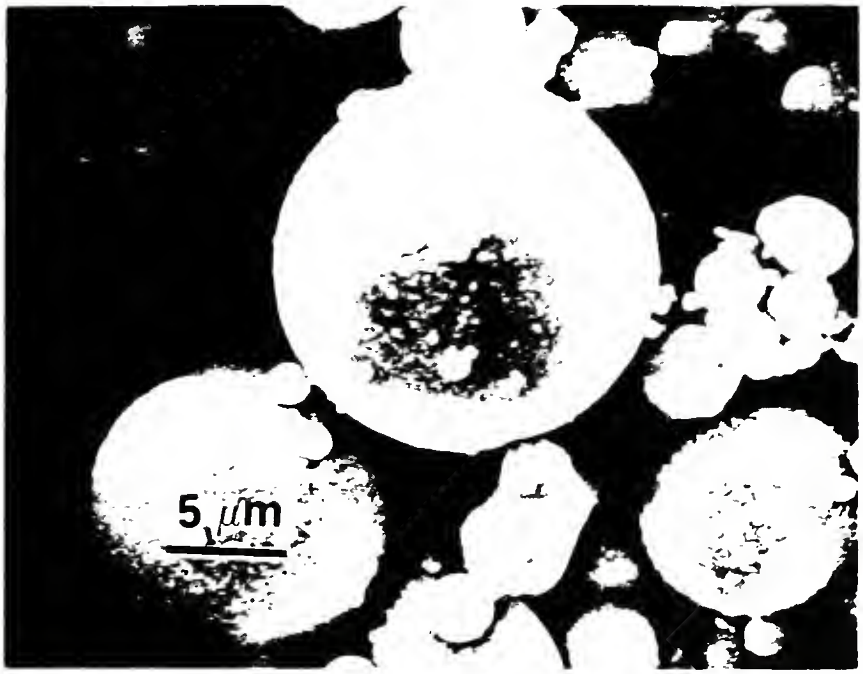
IPL 1 - C. Another area at the same magnification. Most of the fly ash spheres in these and other micrographs of this fly ash show relatively smooth surfaces, but at close range a faint dimpled character can be seen, and occasional spheres like the one in the lower right portion have a fairly textured or "decorated" surface.

IPL 1 - D. This final micrograph, taken at low magnification, shows one of the very large grains representative of oversized material, in this case a complex grain in which an relatively unburned coal fragment entraps hundreds of tiny fly ash spheres. The undesirability of such material in fly ash for use in concrete is evident.

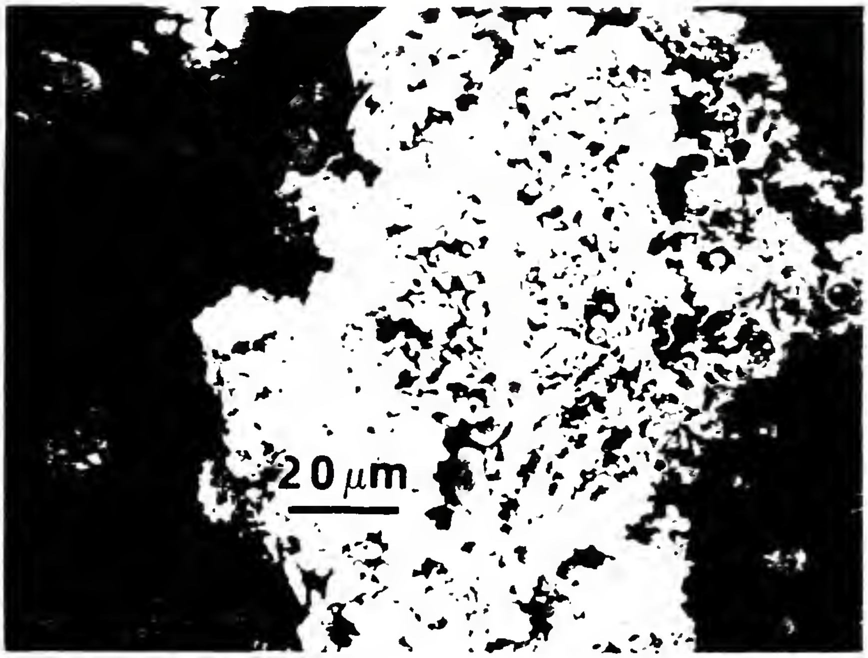
IPL 1 - A Magnification: 1500x.



IPL 1 - B Magnification: 3000x.



IPL 1 - C Magnification: 3000x.



IPL 1 - D Magnification: 700x.

(2) Overall Interpretation

The scanning electron micrographs show a relatively common microstructure for Class F fly ashes. The particles are primarily fairly smooth spheres of an appropriate range of sizes, with some incompletely rounded grains, and in this case some rather oversize particles as well. What little unburned carbon there is seems to be concentrated in these oversize particles, few or no smaller pieces of relict carbon being detected.

No evidence of cenospheres or other hollow grains was detected, except for the apparently hollow pockets in the incompletely rounded grain of the first micrograph.

Results of Pozzolanic Index Test With Cement

Trials carried out with this fly ash using cement "A" gave an only adequate response in the standard pozzolanic index test, the strength recorded being 71% of that of the control mortar. The results obtained in the straight 30% weight replacement test (with no adjustment in water content) was a much more encouraging 105% of the control mortar. The discrepancy in results between the two types of test is not due to adjustment of water content in the standard test, since the water demand was actually reduced about 7% by the presence of the fly ash.

Summary Characterization

This fly ash is a reasonably typical low calcium Class F fly ash, with a modest alkali and sulfate content but a rather high MgO content. It appears to have a somewhat high content of oversized material. Nevertheless the carbon content is quite low. The content of magnetic

particles is very high, and since many or most of these would be non-reactive in concrete, the potential for long-term strength gain with this fly ash might be limited.

Fly Ash No. 5: IPL-2

Perry K. Station, Indianapolis Power and Light Co.
Marion County, IN. (Central Indiana)

Introduction

This fly ash was sampled from a silo serving this very small (45 MW) older generating unit in downtown Indianapolis. The unit is operated as a base load generating station, burning an Indiana bituminous coal which has been used continuously for many years.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 10YR 5/1. The verbal equivalent is "gray".

Chemical Analyses

(1) Total analysis, ignited weight basis:

% CaO	1.13
% SiO_2	43.9
% Al_2O_3	25.3
% Fe_2O_3	20.2
% Na_2O	0.53
% K_2O	2.60
% SO_3	1.13
% MgO	3.92
% P_2O_5	0.30
% TiO_2	1.54
Total	100.6

(2) Parameters derived from above analyses

Total % of $SiO_2 + Al_2O_3 + Fe_2O_3$ 89.4

Total alkalies, as equivalent % Na_2O 2.24

(3) Other analyses

Loss on ignition, ignited wt. basis...........	5.20
% carbon by LECO analysis, ignited wt basis...	4.10
The following are determined on an oven-dry basis:	
% Total SO_3	1.44
% Soluble SO_3................................	0.56
Percentage of the total SO_3 that is soluble....	39%
% Soluble Na_2O................................	0.02
% Soluble K_2O................................	0.12
% Total alkalies, as equiv. % Na_2O............	2.13
% Soluble alkalies, as equiv. % Na_2O..........	0.10
Percentage of the alkalies that are soluble.....	5%

(4) Chemical analysis interpretations

The chemical composition of this Class F fly ash appears to be very similar to that of the IPL-1 ash, probably due to the similarity of coal source. The combined SiO_2 + Al_2O_3 + Fe_2O_3 content is again about 90%, and no significant amount of CaO is present. The sulfate content is again about 1%, with a little less than half of it immediately soluble; the alkali content is about 2%, with almost none of it soluble. The MgO content is lower than that of the previous fly ash, but on the other hand, the residual carbon content is significantly higher, amounting over 4%.

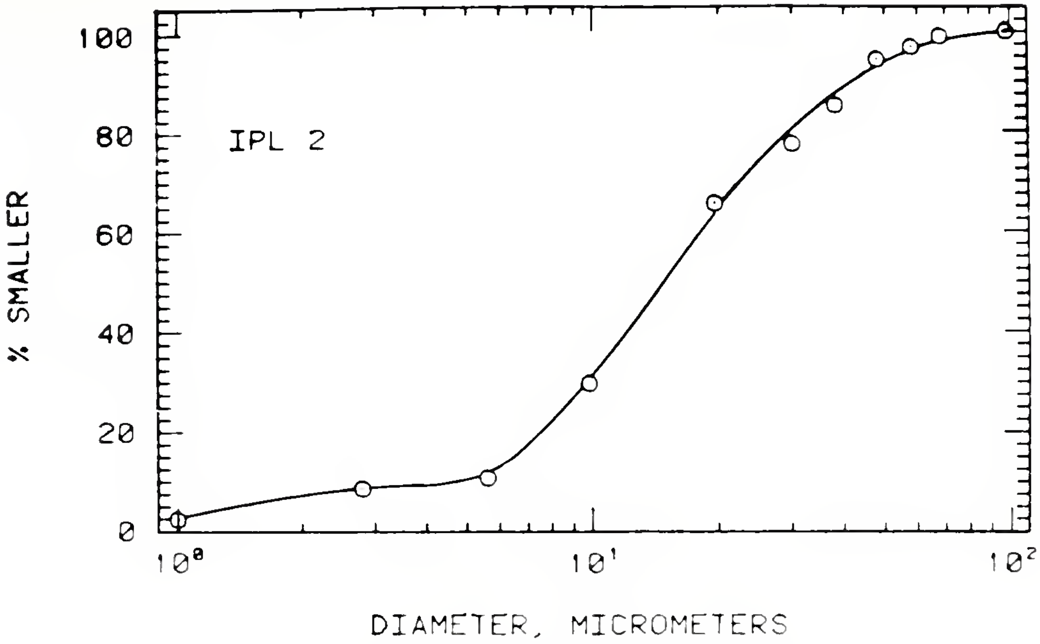
Physical Characteristics

(1) Particle size parameters

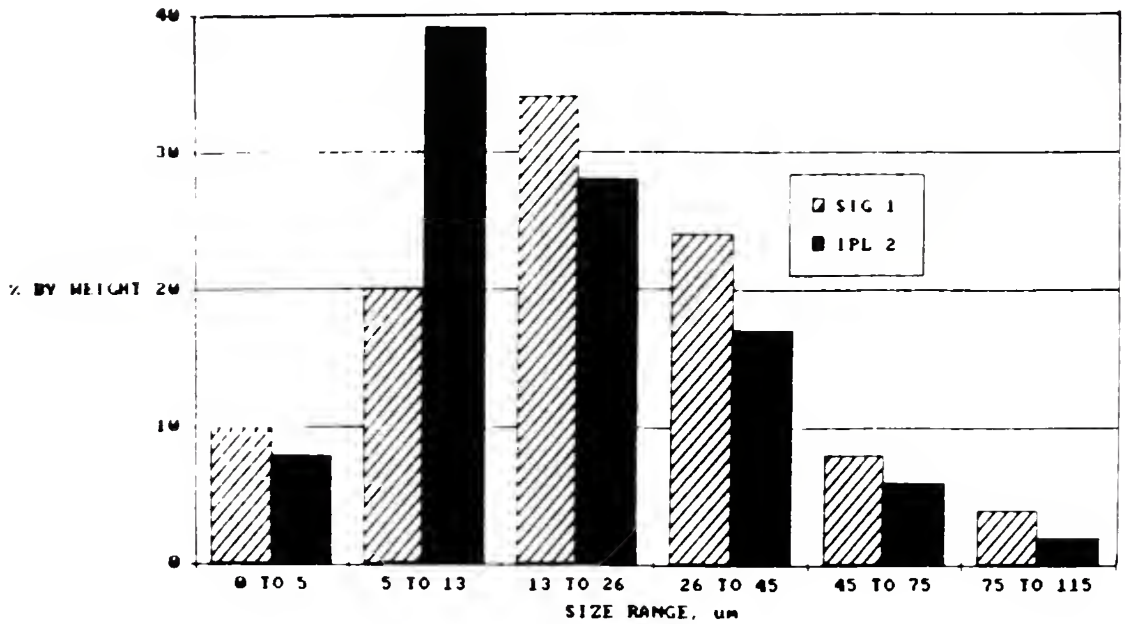
(a) Mean particle size........................ 15 µm

(b) % > No. 325 sieve (45 µm)................ 8 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Particle size distribution interpretation

In contrast to the chemical similarity found between the present fly ash and IPL-1, there is a great difference in the particle size

distributions. The present fly ash is much finer, with a mean size (8 μm) only half that of IPL-1; it is also significantly finer than the SIG-1 fly ash used as the "typical" fly ash for comparison purposes.

Examination of the bar chart indicates that despite this overall fineness, in this fly ash the largest content of particles is not in the finest size class (below 5 μm), but rather in the 5 to 13 μm size class. It is also apparent from the chart that in marked contrast to the IPL-1 ash, in the present fly ash there is only a low content of oversize particles, that is, particles coarser than 45 μm.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................. 4.1

Surface area as measured by high pressure mercury penetration, m^2/g:.................................. 6.4

Blaine fineness, cm^2/g:..........................3200.

Blaine fineness after ignition at 750°C, cm^2/g......2900.

(b) Interpretation of surface area values:

Despite the finer particle size distribution, both the water vapor surface area and the mercury penetration surface area for this fly ash are almost precisely the same as the corresponding values measured for the IPL-1 ash. The Blaine fineness is a little higher (3200 as compared with 2200). Despite the higher carbon content and correspondingly higher loss on ignition, the effect of the ignition on the measured Blaine fineness is very small, only a slight reduction to 2900 cm^2/g being noted.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.37

Specific gravity as measured by high pressure mercury penetration................................ 2.51

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.59

Specific gravity by gas displacement, using helium pycnometry................................ 2.68

(b) Interpretation:

The agreement is reasonably good among the results for all of the different types of specific gravity measurements used. The overall average value for the four methods is 2.54, which is just about the same as that noted for the IPL-1 fly ash.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured weight content of magnetic particles of this fly ash was 20.6%, which is essentially identical to its analytical content of Fe_2O_3. and only half of that of the IPL-1 ash with similar overall chemical composition. The difference might be associated with the lack of oversize particles in the present fly ash; many oversized particles tend to be magnetic, without necessarily being composed entirely of iron oxides.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: Crystalline components identified on the x-ray diffraction pattern of this fly ash include a high content of quartz (SiO_2); mullite ($3Al_2O_3 \cdot SiO_2$); and small amounts of magnetite (Fe_3O_4) and

maghemite (Fe_2O_3).

(b) Glass: An SiO_2 (tridymite-type) glass band centered at about 24° 2Θ (Cu radiation) was found for this fly ash.

(c) Separated magnetic fraction: The x-ray diffraction pattern for the separated magnetic fraction of this fly ash included well-defined peaks for magnetite (Fe_3O_4), hematite (Fe_2O_3), maghemite (Fe_2O_3), and a small content of quartz (SiO_2). There was no indication of any glass band.

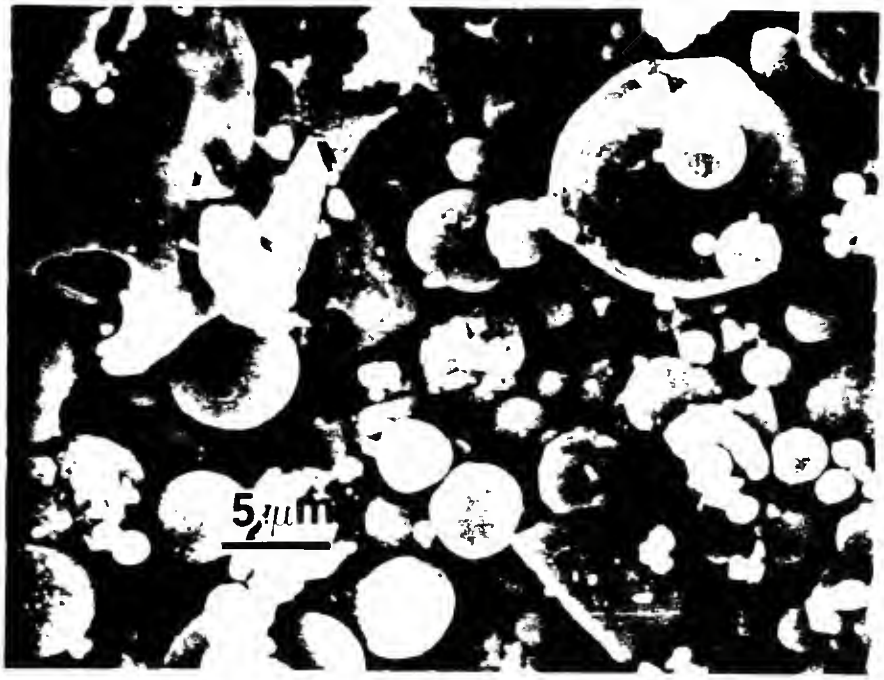
Scanning Electron Micrographs

A set of four of the micrographs were chosen as representative of those secured from this fly ash, and are described below.

(1) Description of Micrographs

IPL 2 - A. This micrograph shows one of the relatively rare areas where nearly all of the particles are spherical. Even here the spherical particles are not exclusive, but one also can find incompletely rounded grains, and near the top center, a group of small fragments of residual carbon. The spheres are relatively smooth surfaced.

IPL 2 - B. A somewhat more typical area. This micrograph was taken at relatively low magnification to show a variety of particles of the various kinds that occur in this fly ash. In addition to the presumably solid spheres, there is at least one visible "plerosphere" - a hollow sphere with smaller spheres included inside of it. Just above it, there is also an incompletely rounded particle which appears to be at least partly hollow. The large, squared-off solid grains near the top of the figure are presumably residual carbon. Carbon particles are also present with tiny fly ash spheres embedded in them, or else spherical holes. There is also a large bloated empty grain at the right side of the figure.



IPL 2 - A Magnification: 3000x.

IPL 2 - B Magnification: 1000x.

IPL 2 - C. Another field at slightly higher magnification. Note the relatively fine, mostly smooth fly ash spheres that predominate here. The large twisted vertical sheet near the center is unburned carbon residue, as is the fragment in the upper right corner that resembles a small piece of Swiss cheese with large holes.

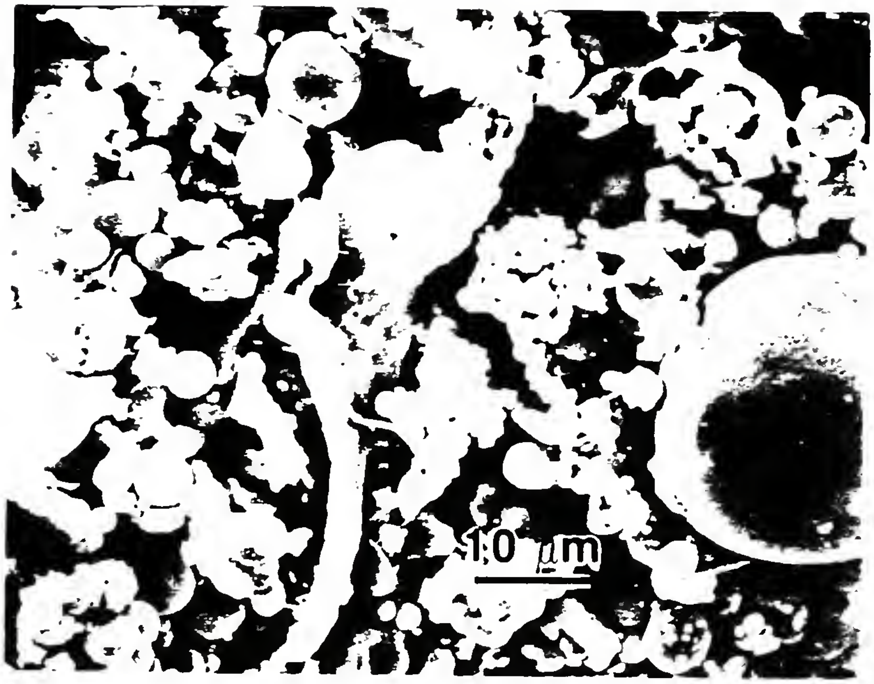
IPL 2 - D. This micrograph, again taken at the same magnification, shows as its focal point a thin curved sheet of residual carbon; this is a good example of the "Swiss cheese" morphology, since many of the fine fly ash spheres that were originally embedded have shaken loose to reveal the holes in which they were apparently formed.

(2) Overall Interpretation

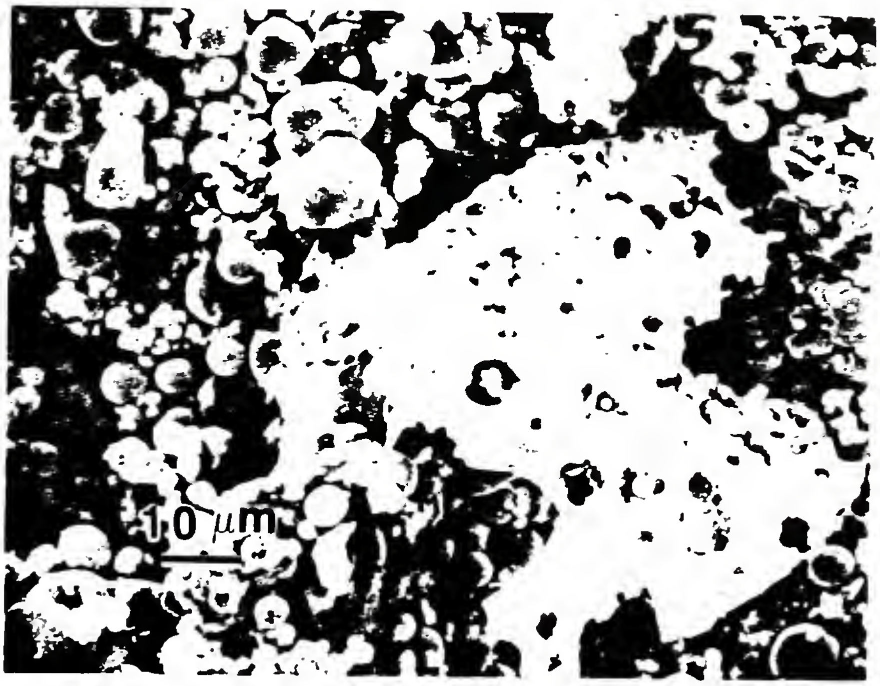
The scanning electron micrographs confirm that this is a relatively fine fly ash, with large numbers of smooth, relatively fine spheres. They also show a substantial number of residual carbon fragments in various morphologies; a number of particles that were not fully rounded, presumably due to incomplete melting; and some hollow particles. This is a fairly typical appearance for Class F fly ashes produced in older plants.

Results of Pozzolanic Index Test With Cement

The pattern of pozzolanic index test results for this fly ash is quite different from those previously discussed. The standard test with cement "A" yielded a fairly satisfactory value of 80%; with cement "B" the value was an almost identical 79%. The supplemental tests carried out on a straight 30% weight replacement basis without water adjustment yielded much poorer results: 59% for cement "A" and 58% for cement "B". This is true despite the increased water demand induced by the fly ash, which in the



IPL 2 - C Magnification: 1500x.



IPL 2 - D Magnification: 1000x.

standard testing required a 4% increase in the water content compared to that of the reference mortar.

Summary Characterization

This fly ash is chemically similar to IPL-1 in being a low calcium Class F fly ash with modest alkali and sulfate contents. However it is much different in terms of size distribution, being basically a fine ash with only a modest content of oversized material. At least as important, it has a substantial content of unburned carbon, which appears as fragments of various forms throughout the different size ranges. It would seem satisfactory for concrete if one judged from the standard pozzolanic index test, but the supplemental testing seems to indicate some difficulty in potential reactivity.

Fly Ash No. 6: PSI-1

Wabash River Station, Public Service Indiana, Inc.
Vigo County IN (Central Indiana)

Introduction

This fly ash was sampled directly from hoppers serving Unit No.2 in this large (760 MW) station. The coal burned here is an Indiana bituminous coal which has been used for many years; occasionally a small amount of additional spot coal is also burned. The ash, definitely a Class F material, was not being marketed commercially at the time of sampling.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 6/2. The verbal equivalent is "light olive gray".

Chemical Analyses

(1) Total analysis, ignited weight basis:

% CaO	2.3
% SiO_2	52.7
% Al_2O_3	21.9
% Fe_2O_3	16.4
% Na_2O	0.32
% K_2O	2.70
% SO_3	1.08
% MgO	1.13
% P_2O_5	0.39
% TiO_2	1.34
Total	100.0

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3.............. 91.0

Total alkalies, as equivalent % Na_2O.......... 2.09

(3) Other analyses

Loss on ignition, ignited wt. basis	1.04
% carbon by LECO analysis, ignited wt basis	0.49
The following are determined on an oven-dry basis:	
% Total SO_3	1.24
% Soluble SO_3	0.66
Percentage of the total SO_3 that is soluble	53%
% Soluble Na_2O	0.09
% Soluble K_2O	0.08
% Total alkalies, as equiv. % Na_2O	2.09
% Soluble alkalies, as equivalent % Na_2O	0.14
Percentage of the alkalies that are soluble	7%

(4) Chemical analysis interpretations

This is a fairly typical or average Class F fly ash in most respects. The combined SiO_2 + Al_2O_3 + Fe_2O_3 content is high, over 90%. The alkali content is moderate, at 2%, with practically none of it soluble. The sulfate content is also low at a little more than 1%. The carbon content is also no problem, with the loss on ignition only slightly over 1%, only half of which is carbon.

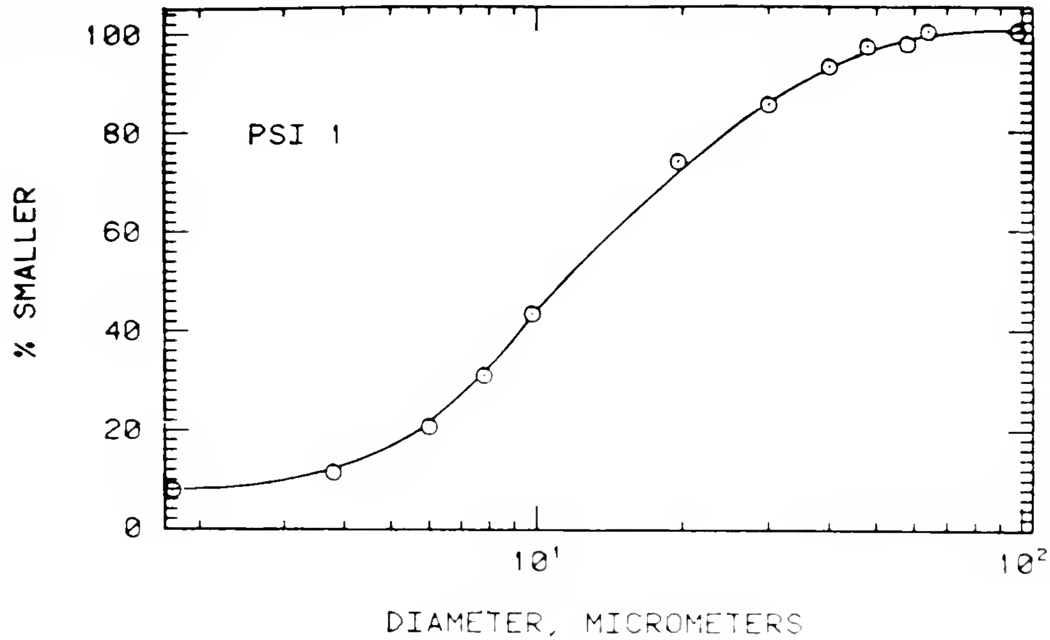
Physical Characteristics

(1) Particle size parameters

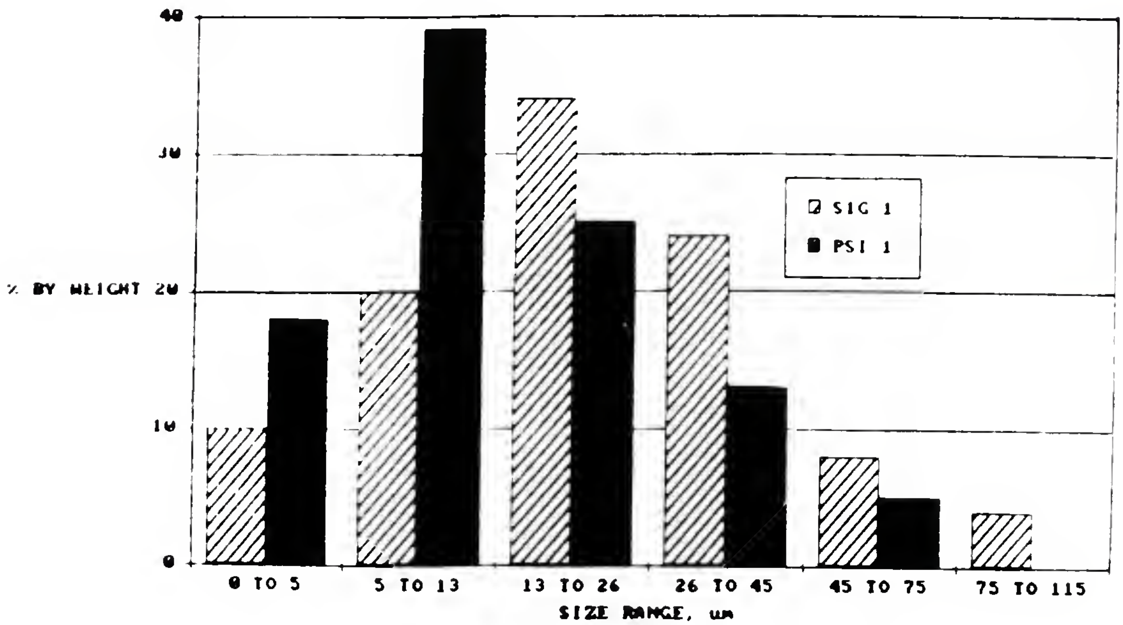
(a) Mean particle size.......................... 11 μm

(b) % > No. 325 sieve (45 μm)................ 5 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Particle size distribution interpretation

This is another relatively fine fly ash, with a mean size of about 11 µm and only about 5% coarser than 45 µm. The bar chart shows that the

general distribution pattern departs from that of the "typical" SIG-1 fly ash in that there is somewhat less coarse material, but almost twice as much material in each of the two finer size ranges, 0 to 5 μm and 5 to 13μm. This would appear to be an almost optimum size distribution for most purposes.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g:.................. 4.7

Surface area as measured by high pressure mercury penetration, m^2/g.................................. 3.9

Blaine fineness, cm^2/g............................2900.

Blaine fineness after ignition at 750°C, cm^2/g......2700.

(b) Interpretation of surface area values:

The surface areas recorded for the water vapor adsorption method agrees reasonably well with that determined by the mercury penetration method. The value, about 4 m^2/g, is on the high side as compared with most fly ashes, as might be expected from the particle size characteristics. The Blaine fineness, around 2900, is only around average. As expected from the relative lack of carbon, the fineness does not change appreciably following ignition.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene........ 2.43

Specific gravity as measured by high pressure mercury penetration................................ 2.24

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.42

Specific gravity by gas displacement, using helium pycnometry................................ 2.47

(b) Interpretation:

This fly ash has quite a low specific gravity as indicated by the trend of the values listed above, all of which are reasonably close to 2.4. Usually such a low specific gravity would be taken as indicating the presence of an appreciable content of hollow spheres. This is especially so when the iron oxide content is reasonably high, as it is in this fly ash (16%).

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured weight content of magnetic particles of this fly ash was 19.5% , which is roughly commensurate with its analytical content of Fe_2O_3 which is 16%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash yielded peaks for quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$) and some magnetite (Fe_3O_4). The is the typical Class F fly ash assemblage of crystalline components.

(b) Glass: The glass band was centered around a maximum near 24° 2Θ (Cu radiation), the usual position for silica (tridymite-type) glass slightly displaced in response to a modest CaO content.

(c) Separated magnetic fraction: X-Ray diffraction of the separated magnetic fraction showed very strong peaks for maghemite (Fe_2O_3) and hematite (Fe_2O_3), and some magnetite (Fe_3O_4) and quartz (SiO_2). There was no recognizable glass band in the pattern.

Scanning Electron Micrographs

Four of the micrographs taken of this fly ash were selected as being representative, and are described below.

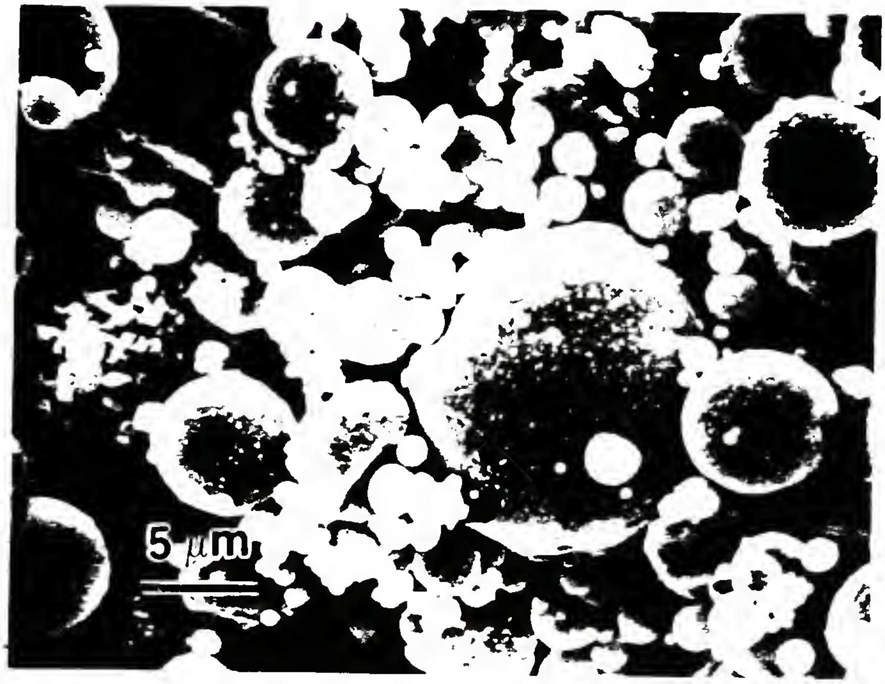
(1) Description of Micrographs

PSI 1 - A. This micrograph shows a reasonably typical field, consisting almost entirely of spherical particles of fly ash, most of them reasonably fine. The surface texture is quite smooth, as is characteristic of many Class F ashes.

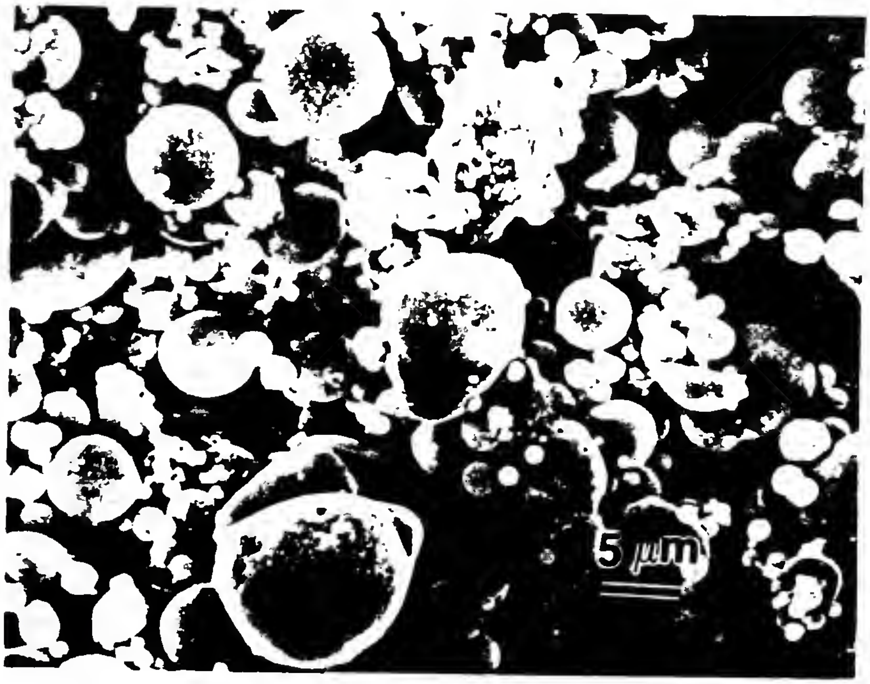
PSI 1 - B. This is a similar field, except that in this one there are a few incompletely-rounded fly ash particles. There are indications that both the slightly elongated particle in the center of the figure and the slightly pointed grain near the bottom are partly hollow.

PSI 1 - C. There is no doubt about this one! The large, thin-walled hollow sphere in the center of the figure shows up very clearly as a "plerosphere" - a hollow sphere containing smaller spheres within it.

PSI 1 - D. This micrograph shows an unusual area for this fly ash in that a large relic of an incompletely-burned coal fragment is present (left side of the figure). It appears that some of the bulges in this grain are enclosed fly ash spheres. The featureless glue holding the fragment together must be residual carbon.

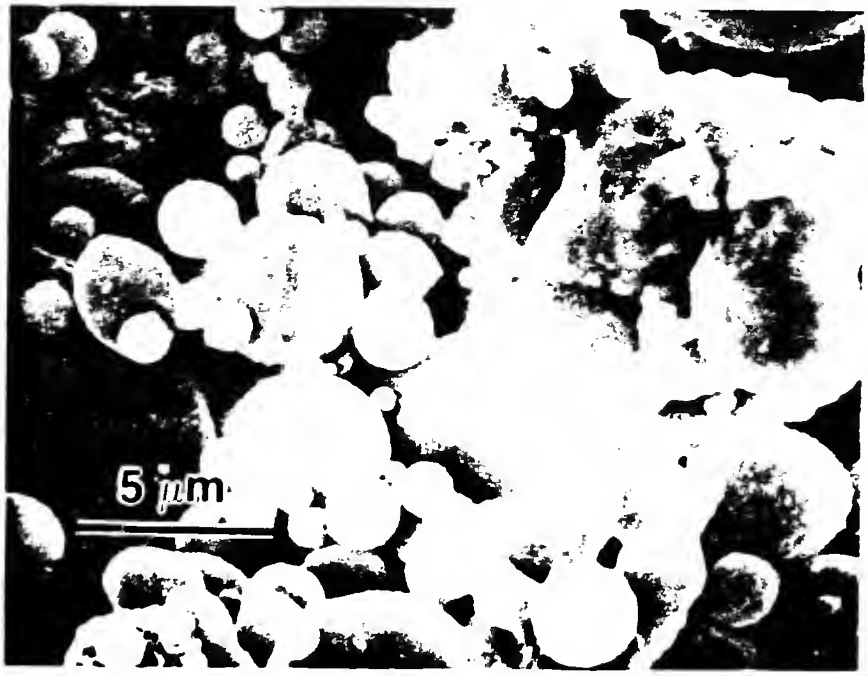


PSI 1 - A Magnification: 3000x.



PSI 1 - B Magnification: 2000x.

PSI 1 - C Magnification: 5000x.



PSI 1 - D Magnification: 5000x.

(2) Overall Interpretation

This fly ash is a well formed, very well burned ash that is quite a typical Class F ash produced under proper operating conditions. The surfaces of the particles are smooth. While only a few can be detected by scanning microscopy, there are likely to be a significant number of hollow spheres in this fly ash. Only a token indication of residual carbon-bearing grains are found, in keeping with the low carbon content determined by the LECO analysis.

Results of the Pozzolanic Index Test With Cement

As might be expected from the previous description, the results of the pozzolanic index tests were good. The standard test procedure gave strengths of 80% and 79% respectively, of the strengths of the respective reference mortars, for tests carried out with cements "A" and "B". This was in spite of a slight additional increment of water required by the presence of the fly ash. In the supplementary testing using a straight 30% weight replacement with no adjustment of water content, the strengths were 117% and 113%, respectively, of those of the reference mortars, attesting to the reactivity of the fly ash.

Summary Characterization

It is apparent that this is a superior Class F fly ash. It has a fine size distribution and a low content of alkalies, sulfate, and residual carbon. The percentage of magnetic particles is not excessive. The fly ash is well burned and nearly all the particles are spheres. The strength developed in the pozzolanic index testing, especially at constant water content, is impressive.

Fly Ash No. 7: PSI-2

Gibson Station, Public Service Indiana, Inc.
Gibson County, IN (Southwest Indiana)

Introduction

This fly ash was sampled from the fly ash transfer line serving Units 3 and 4 of this very large generating station. Gibson is the largest generating plant in Indiana, with a rated capacity of 2540 MW in four boiler units. The coal burned is Illinois basin bituminous coal from Indiana and Illinois, the sources having been used for many years. The ash produced is of the Class F, low calcium type. The plant is operated as a base load station for the PSI system. At the time of sampling the ash was not being marketed commercially.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 6/2. The verbal equivalent is "light olive gray".

Chemical Analyses

(1) Total analysis, ignited weight basis:

% CaO	2.8
% SiO_2	51.4
% Al_2O_3	22.1
% Fe_2O_3	17.2
% Na_2O	1.29
% K_2O	2.24
% SO_3	2.08
% MgO	1.40
% P_2O_5	0.49
% TiO_2	0.37
Total	101.4

(2) Parameters derived from above analyses:

Total % of $SiO_2 + Al_2O_3 + Fe_2O_3$...............90.7
Total alkalies, as equivalent % Na_2O.......... 2.76

(3) Other analyses:

Loss on ignition, ignited wt. basis........... 1.20
% carbon by LECO analysis, ignited wt. basis...0.45

The following are determined on an oven-dry basis:

% Total SO_3 ....2.18
% Soluble SO_3..............................0.79
Percentage of the total SO_3 that is soluble.... 36%

% Soluble Na_2O.............................. 0.19
% Soluble K_2O............................... 0.05
% Total alkalies, as equiv. % Na_2O.............2.73
% Soluble alkalies, as equivalent % Na_2O...... 0.22
Percentage of the alkalies that are soluble:.... 8%

(4) Chemical analysis interpretations:

The analytical values determined for this fly ash are almost exact duplicates of those for the PSI 1 ash previously discussed, and are typical for a well-burned fly ash from Illinois basin coal. The combined $SiO_2 + Al_2O_3 + Fe_2O_3$ content is again over 90%. There is a little more sodium than in the previous ash, but again neither the sodium or the potassium present is appreciably soluble. The sulfate content is a bit higher than in the previous fly ash (2%) but again only about a third of it is soluble. The ignition loss and residual carbon content are again very low.

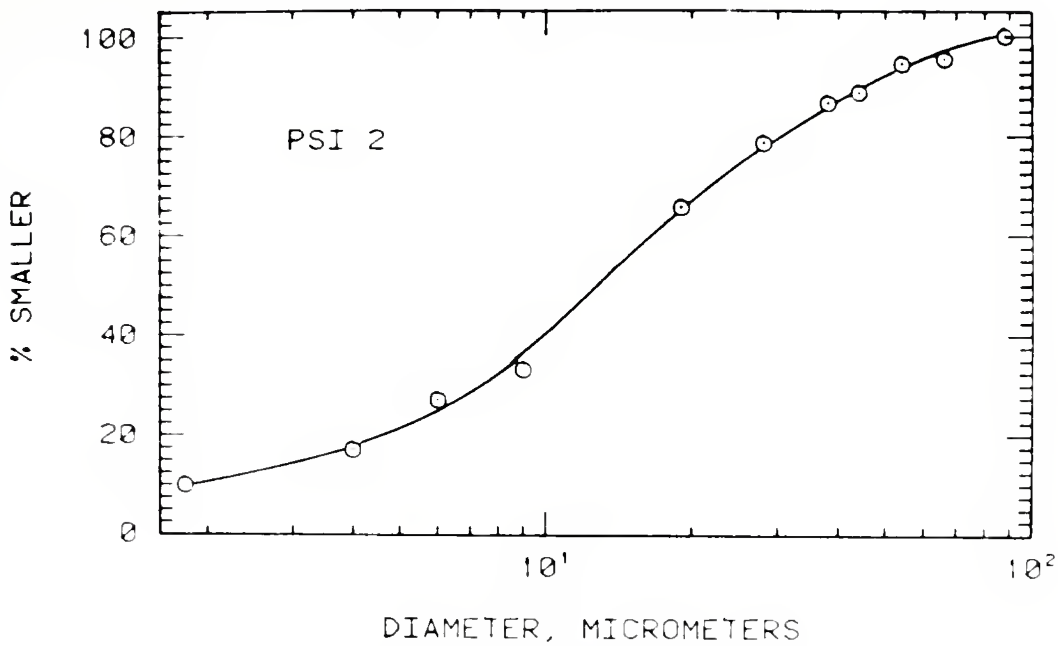
Physical Characteristics

(1) Particle size parameters:

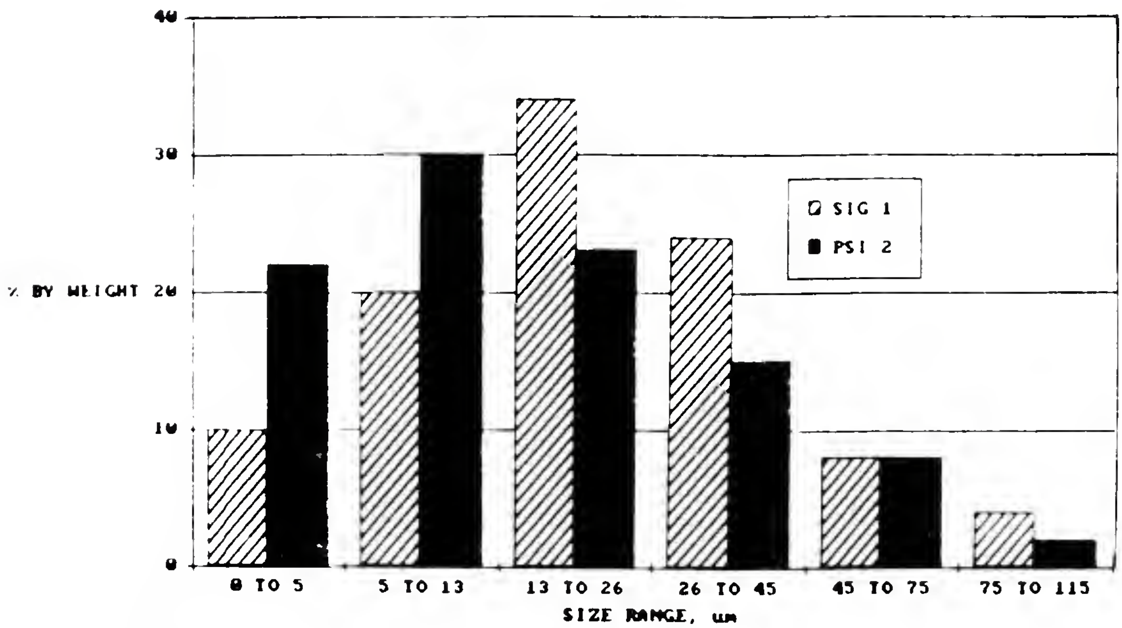
(a) Mean particle size: .... 12 µm

(b) % > No. 325 sieve (45 µ)................ 10 %

(c) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

The particle size distribution of this fly ash is quite similar to that of PSI 1, as the parameters indicate. The mean size is 12 μm as

compared to 11 μm, and the % >45 μm is 10% as compared with 5%. The bar chart shows the relatively fine nature of the size distribution, showing significantly greater percentages in the 0 to 5 μm and 5 to 13 μm size fractions for this fly ash than for the the "typical" SIG-1 comparison fly ash.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................. 4.2

Surface area as measured by high pressure mercury penetration, m^2/g:................................ 6.6

Blaine fineness, cm^2/g:............................2400.

Blaine fineness after ignition at 750°C, cm^2/g......2400.

(b) Interpretation of surface area values:

The surface areas recorded for the water vapor adsorption method is a reasonable 4.2 m^2/g, similar to values obtained on the previous fly ash. However, for some reason the mercury penetration value is almost 50% higher. The Blaine fineness is a perfectly normal 2400 cm^2/g, and is not changed by ignition.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.41

Specific gravity as measured by high pressure mercury penetration.............................. 2.56

Specific gravity by gas displacement, using nitrogen gas pycnometry......................... 2.31

Specific gravity by gas displacement, using helium pycnometry.............................. 2.54

(b) Interpretation:

Again the specific gravity is low, averaging a little over 2.4. By the same reasoning as cited for the previous fly ash, an appreciable content of hollow particles is expected.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

The measured weight content of magnetic particles of this fly ash was 21.1%, essentially the same as for the PSI 1 fly ash, and again roughly commensurate with the analytical content of Fe_2O_3 (in this case 17%).

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash indicated the presence of a moderate amount of quartz (SiO_2) and small amounts of mullite ($3Al_2O_3 \cdot 2SiO_2$), hematite (Fe_2O_3), magnetite (Fe_3O_4), and surprisingly, a possible trace of anhydrite ($CaSO_4$).

(b) Glass: The glass band appeared to be relatively intense in this x-ray pattern, indicative of a larger glass content than usual. The band had its maximum at about 24° 2Θ (Cu radiation), indicative of the usual SiO_2 (tridymite-type) glass structure.

(c) Separated magnetic particles: The crystalline components found in the x-ray diffraction pattern of the magnetically-separated portion of the fly ash were maghemite (Fe_2O_3), hematite (Fe_2O_3), magnetite (Fe_3O_4), and a very small amount of quartz. There was no indication of a glass band in the background level of the pattern.

Scanning Electron Micrographs

Again four micrographs were chosen as representative of the larger set taken in this work. Their description is provided below.

(1) Description of Micrographs

PSI 2 - A. This micrograph illustrates the general shape and part of the size range of the particles of this fly ash. Nearly all the particles are spherical, and with a few exceptions, smooth-textured.

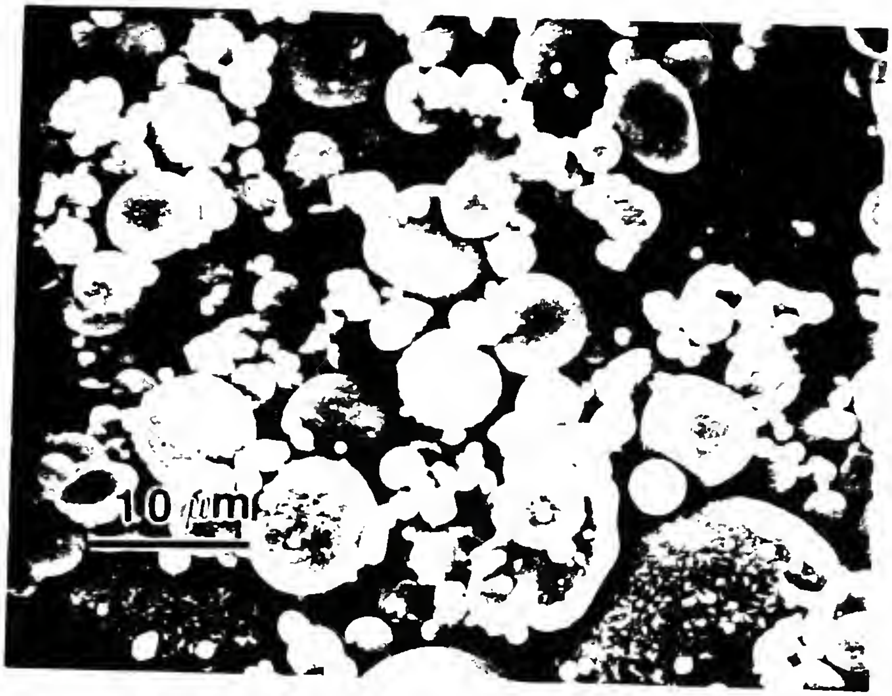
PSI 2 - B. Another typical area, with a somewhat greater disparity of sizes of spheres apparent. Note the slightly roughened or foliated areas on parts of the surface of the largest sphere, and the rough texture of the atypical smaller sphere touching it on the right.

PSI 2 - C. An area appearing to show a cluster of tiny spheres still holding together in the upper center portion, with presumably a little bit of unburned carbon still holding the little spheres together. Note also the rough, imperfectly rounded grain below the cluster and the larger dark imperfectly-rounded grain to the right of it.

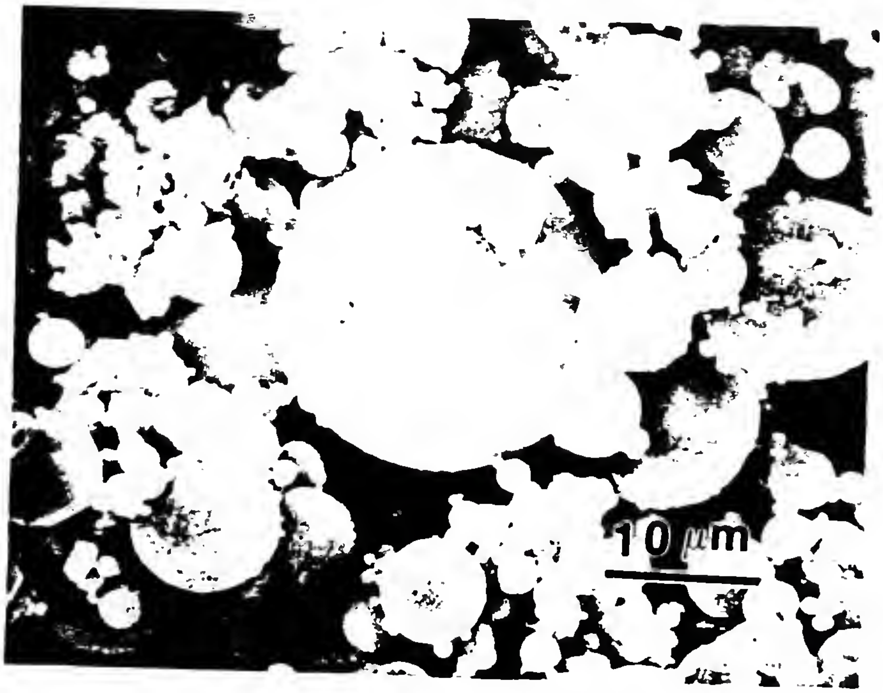
PSI 2 - D. A clearly exposed plerosphere, showing that there are indeed hollow spheres in this fly ash. Note the fairly large gray sphere included inside with the many small bright included spheres.

(2) Overall Interpretation

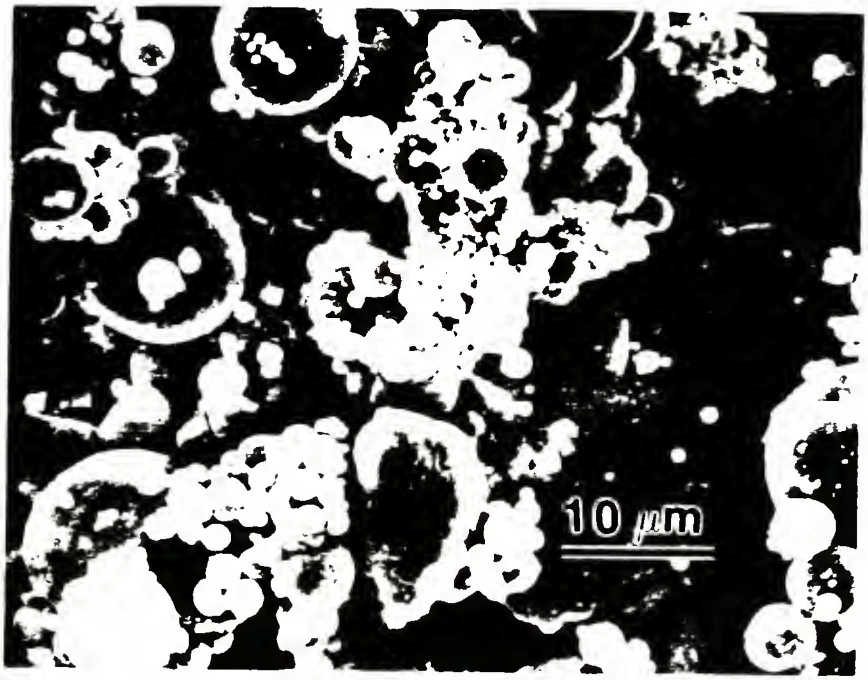
Again, the fly ash depicted here is a well-burned, spherical, clean fly ash with mostly smooth surfaces and some content of hollow spheres.. Very little visible relict carbon is seen; the presence of some is inferred from the occasional clusters of tiny spheres which still cling together, suggesting that a little bit of the carbon has not burned out from between them. This is a "classic" Class F fly ash.



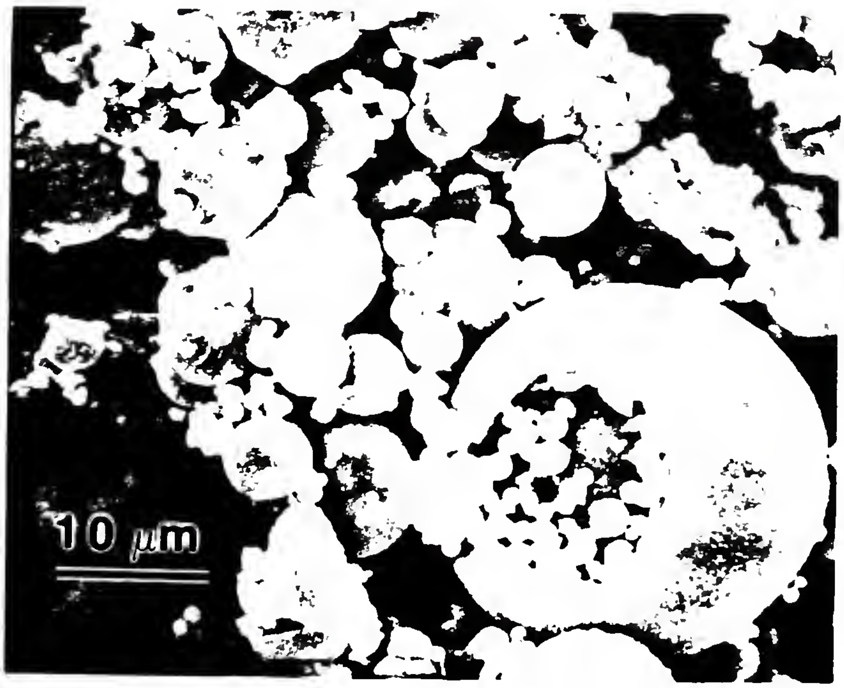
PSI 2 - A Magnification: 2000x.



PSI 2 - B Magnification: 2000x.



PSI 2 - C Magnification: 2000x.



PSI 2 - D Magnification: 2000x.

Results of Pozzanic Index Test With Cement

The standard pozzolanic index tests gave excellent results with this fly ash, the values with cement "A" being 87% and with cement "B" 90%. However, it appears that this rather good performance is primarily a response to the reduced water demand rather than an indication of reactivity. The fly ash mix had a water demand for the necessary flow which was about 15% less than that of the reference mortar. In the supplemental tests carried out on a straight weight replacement basis the strength devloped was only 71% of the strength of the reference mortar for cement "A" and 73% for cement "B".

Summary Characterization

This fly ash is almost identical in many respects to the PSI 1 ash evaluated previously. Like it, the present fly ash is almost a prototype Class F material, with low contents of alkalies, sulfate, and carbon, well rounded smooth spheres, some hollow grains, and a significant proportion of magnetic particles. The pozzolanic index test response is good, apparently due more to reduced water requirement than to superior reactivity.

Fly Ash No. 8: PSI-3

R. A. Gallegher Station, Public Service Indiana, Inc.
Floyd County, IN (Southeast Indiana)

Introduction

This fly ash was sampled directly from the hoppers below three separate precipitators (front and rear banks) of this medium sized (560 MW) station in Southeastern Indiana. The coal burned is an Indiana bituminous coal which has been used for many years and is planned to continue being used for the indefinite future. Gallegher Station is said to be operated as a base load station. The ash was not marketed commercially at the time of sampling, but there were plans for future marketing as a Class F fly ash.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 3/1. The verbal equivalent is "very dark gray".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	6.9
% SiO_2	41.8
% Al_2O_3	21.2
% Fe_2O_3	17.2
% Na_2O	0.57
% K_2O	2.10
% SO_3	1.60
% MgO	3.10
% P_2O_5	0.47
% TiO_2	0.81
Total	95.8

(2) Parameters derived from above analyses:

Total % of SiO_2 + Al_2O_3 + Fe_2O_3...............80.2
Total alkalies, as equivalent % Na_2O.......... 1.95

(3) Other analyses:

Loss on ignition, ignited wt. basis.......... 10.0
% carbon by LECO analysis, ignited wt. basis...9.2

The following are determined on an oven-dry basis:

% Total SO_3 ....1.97
% Soluble SO_3.................................0.57
Percentage of the total SO_3 that is soluble.... 29%

% Soluble Na_2O................................ 0.08
% Soluble K_2O................................. 0.04
% Total alkalies, as equiv. % Na_2O.............2.14
% Soluble alkalies, as equivalent % Na_2O...... 0.11
Percentage of the alkalies that are soluble:.... 5%

(4) Chemical analysis interpretations:

The above analyses would result in classification of this fly ash properly as an ASTM Class F fly ash, since the total of the SiO_2 + Al_2O_3 + Fe_2O_3 contents is 80%, over the minimum required. Nevertheless, the relatively high CaO content (7%) makes it unusual for such fly ashes. The alkali content and sulfur content are both moderate, and the alkalies are essentially insoluble, as is typical for most Class F materials. What is unusual about this fly ash is the very high content of unburned carbon, almost 10%, which may interfere in the plans for its utilization, at least in concrete.

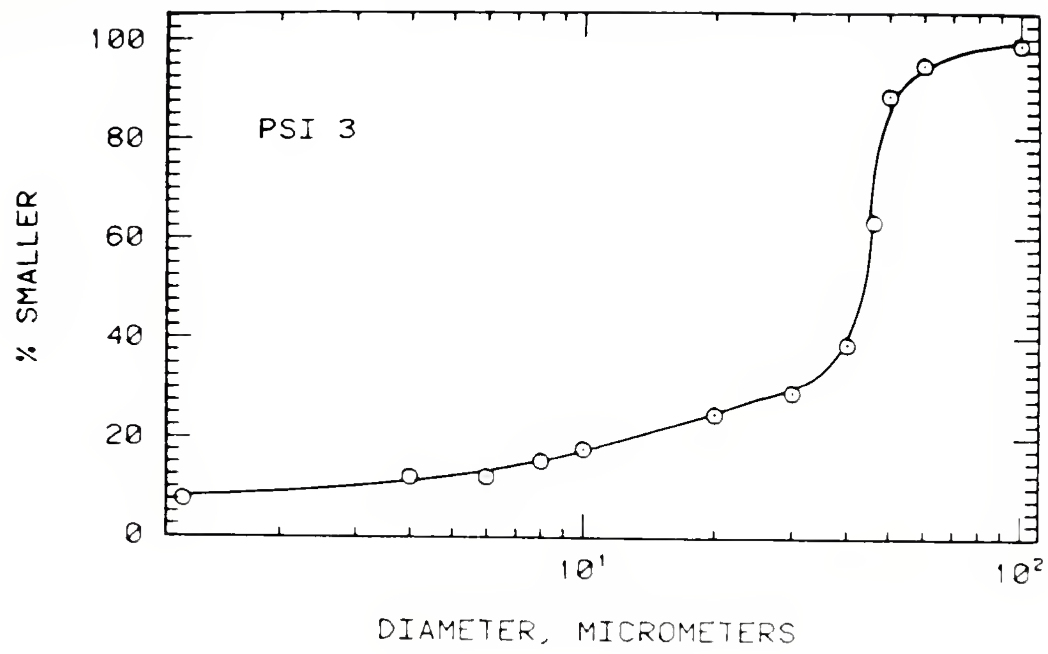
Physical Characteristics

(1) Particle size parameters:

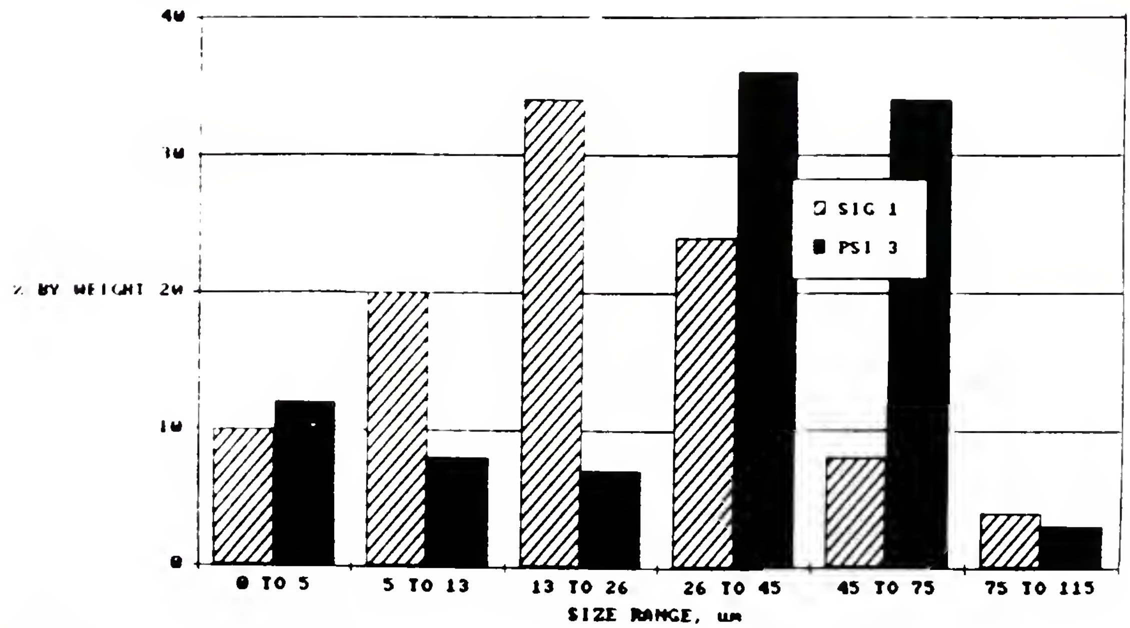
(a) Mean particle size: .... 43 μm

(b) % > No. 325 sieve (45 μ)................ 37 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



As is evident from the mean size (43 μm), the large content of oversize particles (37% > 45 μm), and the particle size distribution curve, this is

a much coarser fly ash than the ones previously examined. The bar chart shows that the size distribution is a rather peculiar one, at least as compared to the "typical" SIG-1 fly ash. There is a reasonable content of particles in the very finest size range, but a severe shortage of particles in the 5 to 13 μm and 13 to 26 μm size ranges. This is accompanied by a modest excess of particles in the next range, 26 to 45 μm, and a very large excess in the 40 to 75 μm range. Surprisingly, there are actually few particles in the coarsest size range, i.e. over 75 μm. The reason for this rather peculiar size distribution is not apparent.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g:.................. 6.8

Surface area as measured by high pressure mercury penetration, m^2/g:................................ 7.0

Blaine fineness, cm^2/g:..........................6100.

Blaine fineness after ignition at 750° C, cm^2/g.....4400.

(b) Interpretation of surface area values:

The surface areas recorded for both the water vapor adsorption method and the mercury penetration method are in agreement, both showing a rather high value of around 7 m^2/g. This is unexpected in terms of the size distribution data. The Blaine fineness is also much higher than expected, and at 6100 cm^2/g is higher than any other fly ash except the very fine particle size NIP-1 ash. The scanning electron microscopy investigation provides a partial answer, suggesting that this apparent anomaly may be due to a combination of an unusually fine collection of spheres in the finest size range combined with the presence of some complex, high surface area

coarse grains.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene....... 2.69

Specific gravity as measured by high pressure mercury penetration.............................. 2.30

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.66

Specific gravity by gas displacement, using helium pycnometry............................... 2.79

(b) Interpretation:

Except for the unusually low value recorded for the mercury penetration method, the values center around 2.7, which is higher than that of the previous Class F fly ashes examined, although the iron oxide content is about the same as the others. This suggests a lesser content of hollow spheres, which often accompanies higher CaO contents in fly ash.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash had a fairly high content of magnetic particles, the value recorded being 28.6%. This is more than 1-1/2 times the recorded content of iron oxide.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash indicated the presence of moderate contents of quartz (SiO_2), magnetite (Fe_3O_4), and hematite (Fe_2O_3); a modest, but definite

content of crystalline CaO; and trace contents of mullite ($3Al_2O_3 \cdot 2SiO_2$) and anhydrite ($CaSO_4$).

(b) Glass: The glass band in this pattern was relatively intense and had its maximum at about 26° 2Θ (Cu radiation); this shows the influence of the rather substantial CaO content of the fly ash (almost 7%) on the structure of the glass formed.

(c) Separated magnetic particles:

The crystalline components found in the x-ray diffraction pattern of the magnetically-separated portion of the fly ash were magnetite (Fe_3O_4), hematite (Fe_2O_3), some maghemite (Fe_2O_3), and only a trace of quartz. There was absolutely no glass band detected.

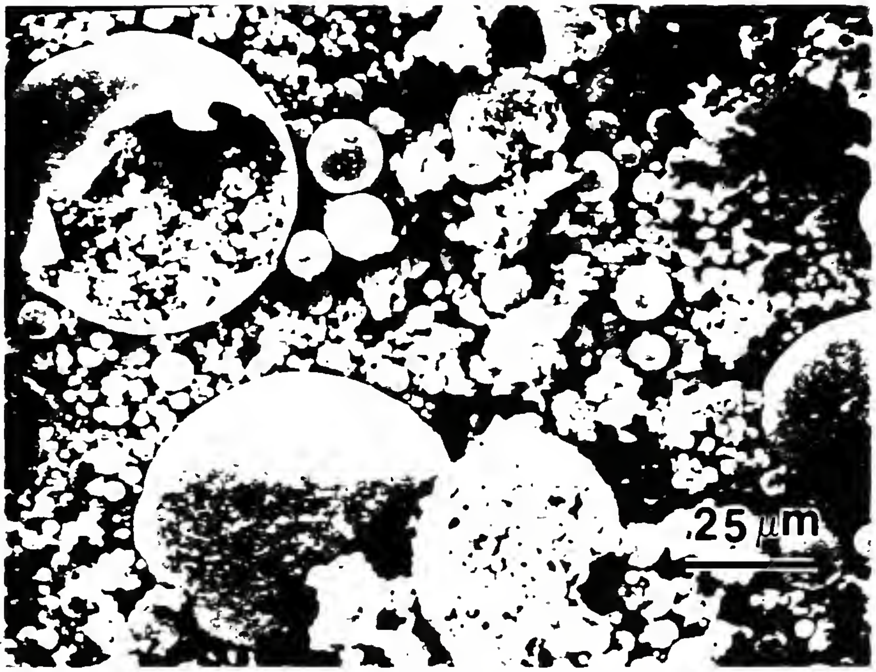
Scanning Electron Micrographs

Again four micrographs were chosen as representative of the larger set taken in this work, and are described below.

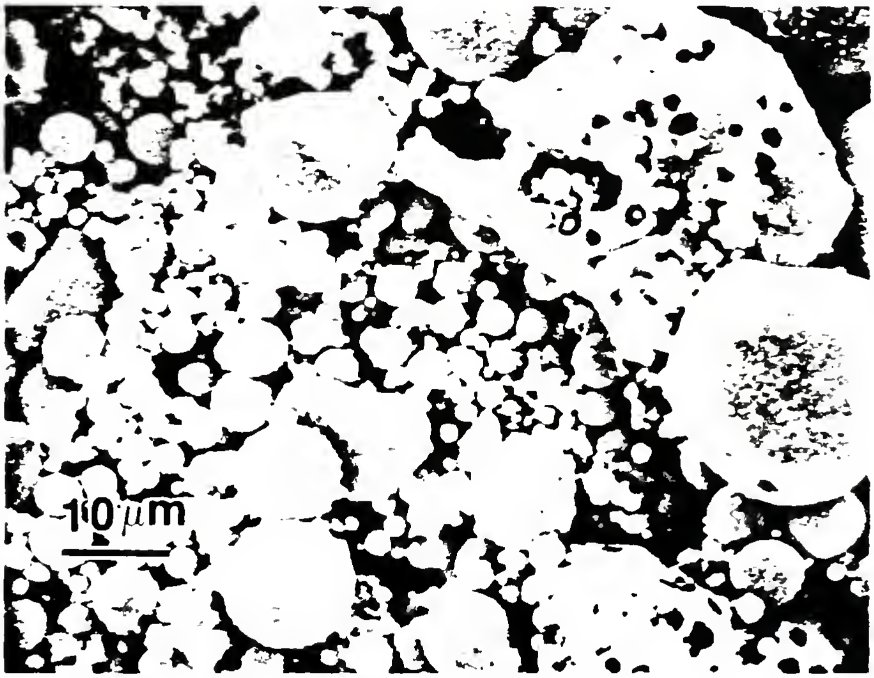
(1) Descriptions of Micrographs

PSI 3 - A. This relatively low-magnification picture, taken at 700x, provides a visual indicationof the peculiar, almost gap-graded size distribution; the shortage of particles between about 5 μm and about 25 μm is manifest. The large open plerosphere in the upper right region is full of tiny spheres. There is a large bright "cluster" grain to the left of the scale marker, with a high content of residual carbon. Other mostly carbon grains appear in the upper left corner and in several other places in the micrograph.

PSI 3 - B. Another typical area; here two large residual carbon "Swiss-cheese" like grains are present, in the top right and bottom right corners respectively. It is also noticeable that some of the spheres seem



PSI 3 - A Magnification: 700x.



PSI 3 - B Magnification: 1500x.

to have at least a moderate surface roughness or surface deposit.

PSI 3 - C. An area showing some of the larger spherical fly ash grains is shown here. The center sphere is extremely rough textured, and has a number of tiny fly ash spheres attached to it. The other spheres are not as rough, but some appear to have some sort of surface deposit on them.

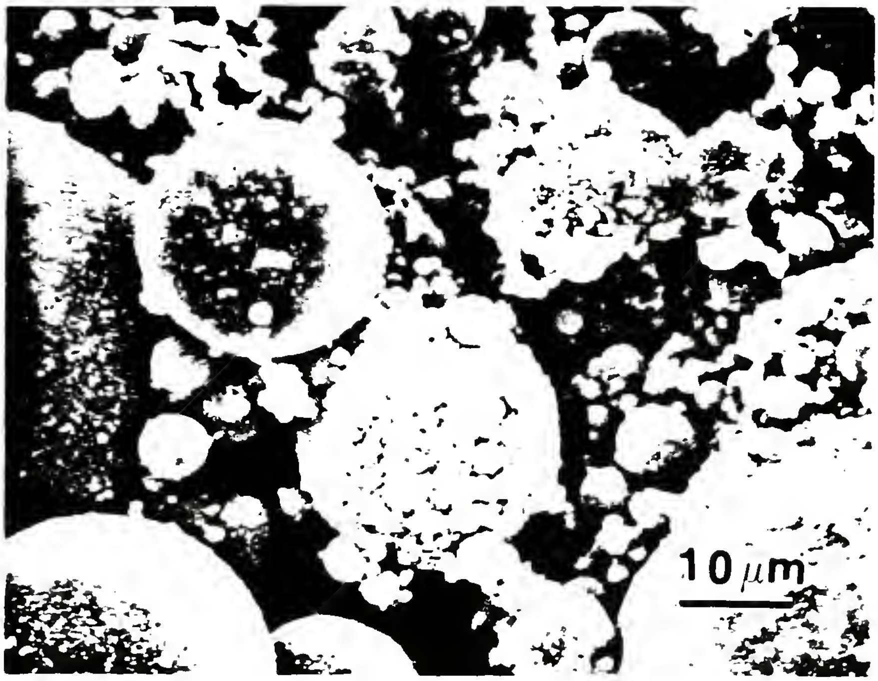
PSI 3 - D A high magnification view showing the surface texture of some typical small and intermediate sized spheres. In this view the surface texture appears to be perhaps a secondary depositon an otherwise smooth surface.

(2) Overall Interpretation

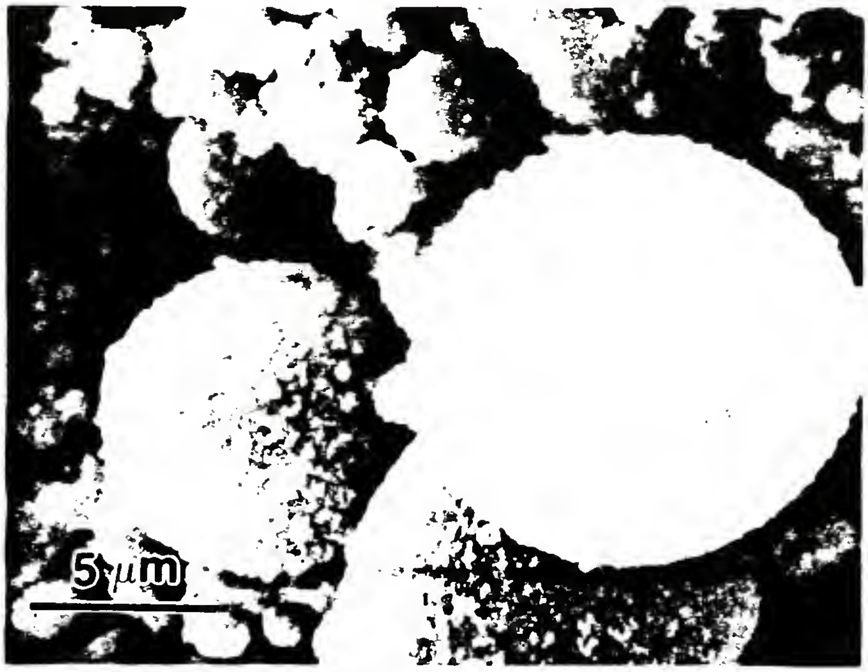
This fly ash is an unusual one for a Class F material. The mineral grains are almost completely spherical, but the spheres show a considerable surface deposit. The size distribution is peculiar, being missing most of what should be the intermediate size range between very small and large spheres. The very high content of residual carbon is evident in carbon grains and in cluster particles with significant residual carbon holding the inorganic spheres together.

Results of Pozzolanic Index Test With Cement

This fly ash did not perform very well on either version of the pozzolanic index test. In the standard test with cement "A" the strength of the fly ash mortar only reached 49 percent of that of the reference cement mortar. There was a substantial increase in water demand associated with this fly ash, the water required to obtain the specified flow being increased by about 15%. However, this was not the only reason for the poor performance, since on the supplementary test with a 30% weight replacement and no water adjustment, the value was a virtually identical 50%.



PSI 3 - C Magnification: 1500x.



PSI 3 - D Magnification: 5000x.

Summary Characterization

This fly ash is a "maverick" in many respects. The content of CaO is high for a Class F fly ash, almost enough to qualify it as an "intermediate" between Class C and Class F. The particle size distribution is peculiar, with a coarse mean size but a significant content of very fine spheres, apparently generating a high surface area. The very high residual carbon content shows up in a significant proportion of particles being carbon, or else in clusters held together by residual carbon. There is also a significant content of magnetic particles, which presumably do not react or react only a little with cement. The apparent lack of reactivity and the high water demand are such that this fly ash would not appear to be a good choice as a component in concrete.

Fly Ash No. 9: SIG-1

A. B. Brown Station, Southern Indiana Gas and Electric Co.
Posey County, IN (Southeast Indiana)

Introduction

This fly ash was sampled directly from the hoppers at Unit 1 of this small (250 MW) but fairly new station located on the Ohio River. The coal burned is bituminous coal from a single source in Indiana, and the expressed plans were to continue the use of that coal for the indefinite future. The station is operated cyclically, mostly at peak load periods. The fly ash being produced, which would be a Class F fly ash, was not marketed commercially at the time of sampling.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 10YR 5/1. The verbal equivalent is "gray".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	2.24
% SiO_2	39.7
% Al_2O_3	27.3
% Fe_2O_3	25.5
% Na_2O	0.43
% K_2O	2.08
% SO_3	0.59
% MgO	1.49
% P_2O_5	0.25
% TiO_2	1.34
Total	100.9

(2) Parameters derived from above analyses

Total % of $SiO_2 + Al_2O_3 + Fe_2O_3$..............92.5

Total alkalies, as equivalent % Na_2O.......... 1.80

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 4.20
% carbon by LECO analysis, ignited wt. basis.. 4.01

The following are determined on an oven-dry basis:

% Total SO_3 .... 0.97
% Soluble SO_3................................ 0.36
Percentage of the total SO_3 that is soluble.... 37%

% Soluble Na_2O.............................. 0.02
% Soluble K_2O............................... 0.08
% Total alkalies, as equiv. % Na_2O............ 1.73
% Soluble alkalies, as equiv. % Na_2O.......... 0.14
Percentage of the alkalies that are soluble:.... 8%

(4) Chemical analysis interpretations

This fly ash is a more nearly typical Class F material in terms of its chemical analysis. The total of the $SiO_2 + Al_2O_3 + Fe_2O_3$ contents is over 90%, and includes a rather high iron content, in excess of 25% Fe_2O_3. The CaO content is a modest 2%. The sulfate content is low, the alkali content at about 2% is moderate, and the alkalies and most of the sulfate are insoluble. The residual carbon content, at 4%, is not excessive by most standards, although it is a bit on the high side.

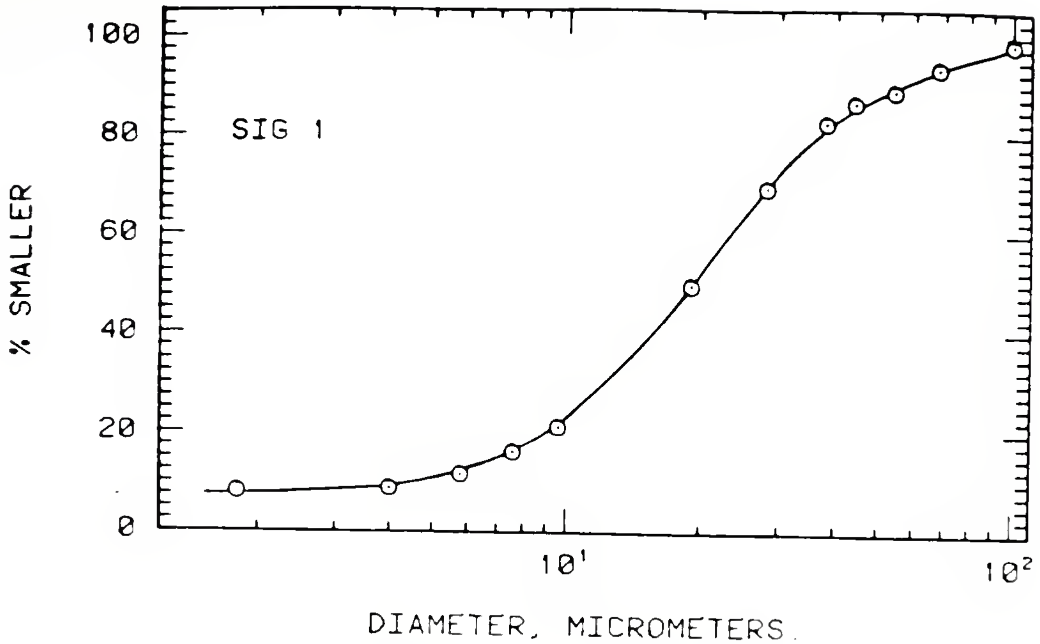
Physical Characteristics

(1) Particle size parameters

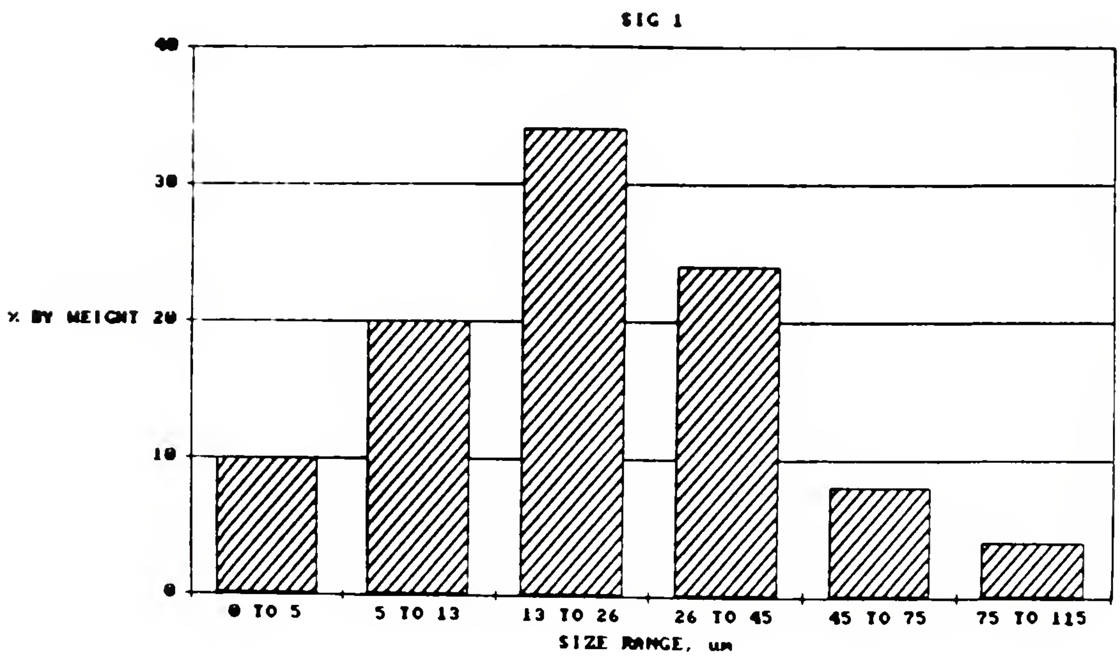
(a) Mean particle size: .... 19 μm

(b) % > No. 325 sieve (45 μm)................ 12 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

This fly ash was selected as the "typical" ash for use in examining the bar chart patterns; as such it is not surprising that the mean size

(19 µm) and the percentage of >45 µm particles (12%) are about average for the whole set of fly ashes. The bar chart plot shows a reasonable distribution of sizes in the different size range groupings used.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g: 3.4

Surface area as measured by high pressure mercury penetration, m^2/g: 13.4

Blaine fineness, cm^2/g: ....2700.

Blaine fineness after ignition at 750°C, cm^2/g......2200.

(b) Interpretation of surface area values

The surface area recorded for the water vapor adsorption method is a reasonable 3.4 m^2/g, but that secured in the mercury penetration procedure is extremely high, 13.4 m^2/g; the reason for the discrepancy is not known. The high value is not due to the presence of the residual carbon, since the fly ash was ignited in a special trial, and after ignition the mercury penetration method yielded a still very high 10.6 m^2/g. The Blaine fineness, 2700 cm^2/g, is about average; it is reduced somewhat by igniting the sample.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene........ 2.40

Specific gravity as measured by high pressure mercury penetration................................ 2.35

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.24

Specific gravity by gas displacement, using helium pycnometry............................... 2.53

(b) Interpretation:

The specific gravity values recorded for this fly ash by the different methods average around 2.4, which is a reasonably low value in view of the relatively high iron content. One might thus expect a significant content of hollow spheres in this ash.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash also had a high content of magnetic particles, the value recorded being 29.5%. However, in this case the content of magnetic particles is roughly the same as the content of analytical Fe_2O_3, which was about 26%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The major crystalline components detected were quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$) as major components, with a little bit of magnetite (Fe_3O_4) and maghemite (Fe_2O_3).

(b) Glass: The glass band in this fly ash is of moderate intensity and is centered around 24° 2Θ (Cu radiation).

(c) Separated magnetic particles: The crystalline components found in the x-ray diffraction pattern of the magnetically-separated portion of the fly ash were magnetite (Fe_3O_4), hematite (Fe_2O_3), some maghemite (Fe_2O_3), some quartz (SiO_2) and a trace of mullite ($3Al_2O_3 \cdot 2SiO_2$). There was absolutely no indication of a glass band in this x-ray pattern.

Scanning Electron Micrographs

The four micrographs discussed below were chosen as representative of those taken of this fly ash.

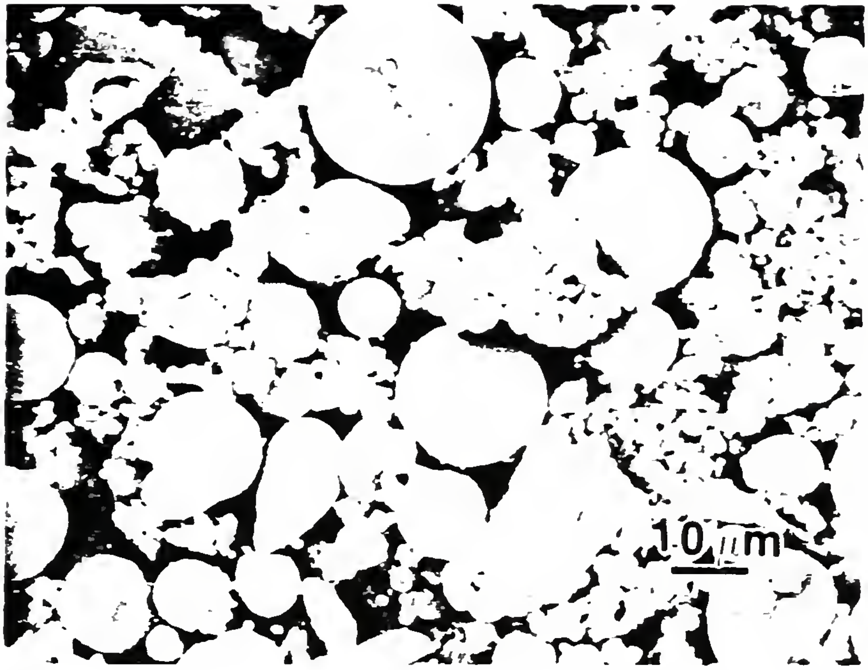
(1) Description of Micrographs

SIG 1 - A. This micrograph shows a quite representative area. There are several different kinds of fly ash particles represented: smooth spheres, a few smooth incompletely rounded grains, a fairly large grain that is not visibly rounded at all (to the left of the scale marker), and a number of 10 to 20 μm clusters of very tiny spheres, presumably held together by unburned carbon.

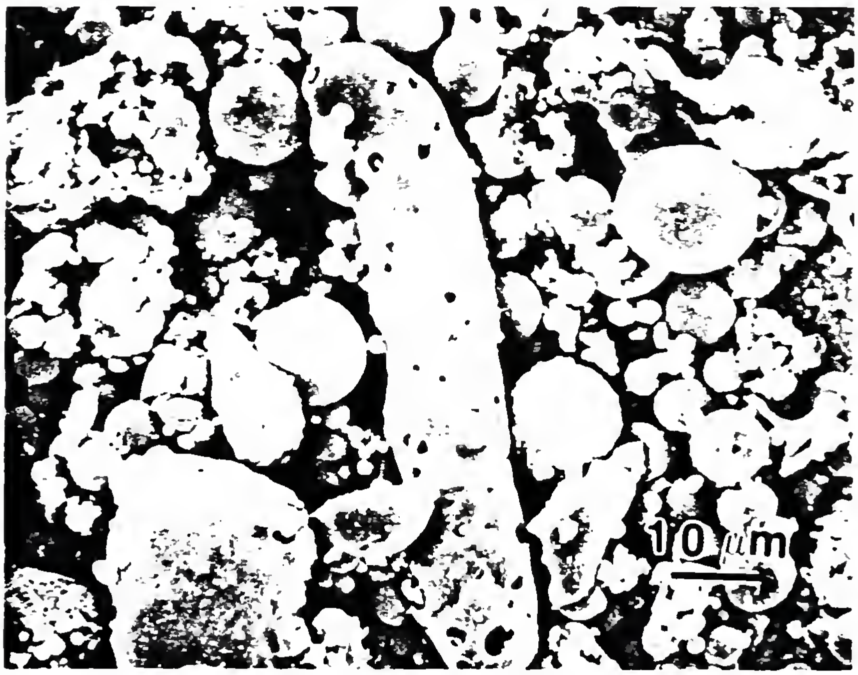
SIG 1 - B. Another area, much like the first, with several additional features. The most prominent is a 70 μm long, worm-like, partly hollow grain running almost the full height of the micrograph. This is an unusual shape for a fly ash grain, but several have been seen. Also noteworthy in this fly ash are (1) a small sphere above the scale designator with an opening in it suggesting its hollow character, and (2) in the upper right a thin, twisted carbon particle.

SIG 1 - C. Another basically similar area, with two kinds of relict carbon visible: a 50 μm long flat-sided stick of coal residue in the lower part of the figure, and several small clusters of tiny fly ash spheres, held together by carbon, in the upper part of the figure.

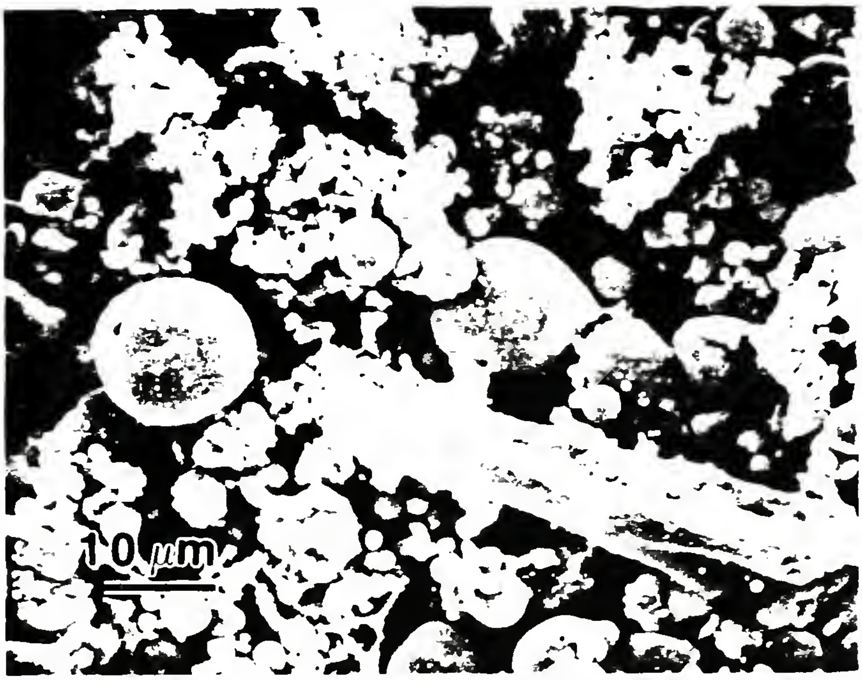
SIG 1 - D A higher magnification view showing certain representative particles of this fly ash in close detail. There are a number of smooth spheres. There is an imperfectly-rounded grain, half-way up the left edge of the figure. There is a "decorated" distorted sphere in the top right quadrant. Most important, there is a clear view of a cluster particle of tiny spheres held together by carbon, occupying the lower right quadrant.



SIG 1 - A Magnification: 1000x.



SIG 1 - B Magnification: 1200x.



SIG 1 - C Magnification: 1500x.

SIG 1 - D Magnification: 3000x.

As seen in the previous micrographs, such cluster grains occur in nearly all parts of the fly ash.

(2) Interpretation

This fly ash seems to be composed of a variety of types of particles: smooth spheres in various sizes (but lacking the finest size range); cluster grains of tiny spheres still entrapped in carbon relicts; and a fair proportion of particles showing holes suggesting they may be partly hollow. The number of the cluster grains is unexpectedly large for this fly ash of not unusually high carbon content.

Results of Pozzolanic Index Test With Cement

This fly ash performed very badly in the standard pozzolanic index testing. The water demand was markedly increased (about 30%!). Apparently in consequence of this remarkable increase in water content, the strength developed with cement "A" was only 31% of the strength of the reference cement mortar. With cement "B" the corresponding figure was a little better, but still only 37%. In the supplemental testing where no adjustment was made of the water content, the results were much more satisfactory. For both cement "A" and cement "B" the values obtained were indentically 73% of the strengths of the respective reference cement mortars.

Summary Characterization

This seems to be a relatively badly burned Class F fly ash with rather normal chemical characteristics, an average particle size distribution, but several unusual and undesirable features: a notably high content of magnetic particles, and a considerable proportion of cluster grains,

relicts of coal fragments comprising tiny spheres held together by small contents of residual carbon, and with lots of internal space. Presumably these particles contribute very much to the excessively high water demand associated with this fly ash. The reactivity, as indicated by strengths developed in the absence of excess water, seems to be adequate.

Fly Ash No. 10: SIG-2

F. B. Culley Station, Southern Indiana Gas and Electric Co.
Warrick County, IN (Southeast Indiana)

Introduction

This fly ash was sampled directly from the hoppers at Unit 3 of this medium-sized (400 MW) station also located on the Ohio River in southeastern Indiana. Several different Indiana bituminous coals are burned here. The station is operated in at least partly a cyclic mode, being used more extensively at peaking periods. The fly ash was not commercially marketed at the time of sampling.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 10YR 5/3. The verbal equivalent is "brown".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	2.59
% SiO_2	39.9
% Al_2O_3	26.4
% Fe_2O_3	24.1
% Na_2O	0.83
% K_2O	2.26
% SO_3	2.12
% MgO	1.89
% P_2O_5	0.19
% TiO_2	1.00
Total	101.3

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3...............90.4
Total alkalies, as equivalent % Na_2O.......... 2.32

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 0.60
% carbon by LECO analysis, ignited wt. basis...0.65

The following are determined on an oven-dry basis:

% Total SO_3 ....2.30
% Soluble SO_3.................................0.84
Percentage of the total SO_3 that is soluble.... 37%

% Soluble Na_2O................................ 0.09
% Soluble K_2O................................. 0.08
% Total alkalies, as equiv. % Na_2O.............2.33
% Soluble alkalies, as equivalent % Na_2O...... 0.14
Percentage of the alkalies that are soluble:.... 6%

(4) Chemical analysis interpretations

This fly ash is a another entirely typical Class F material in terms of its chemical analysis. The total of the SiO_2 + Al_2O_3 + Fe_2O_3 contents is over again 90 %, and again it includes a rather high iron content of about 25% Fe_2O_3. The CaO content is a little over 2-1/2 %. The sulfate content is low, the alkali content at about 2%, is moderate, and the alkalies and most of the sulfate are insoluble. The residual carbon here is quite low, at 0.6%, and thus should not be a factor with this fly ash.

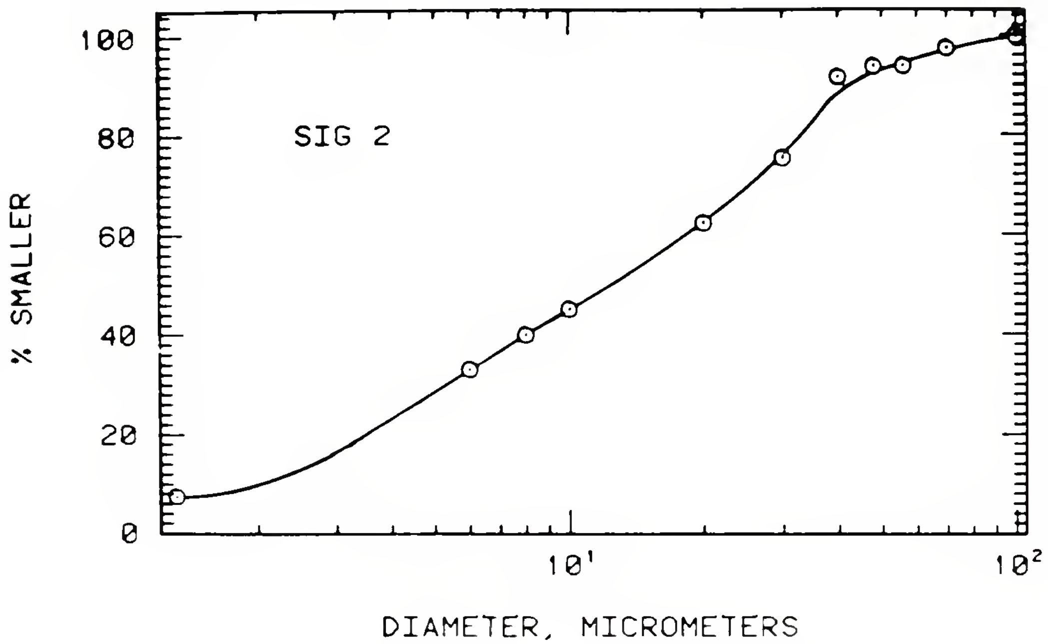
Physical Characteristics

(1) Particle size parameters

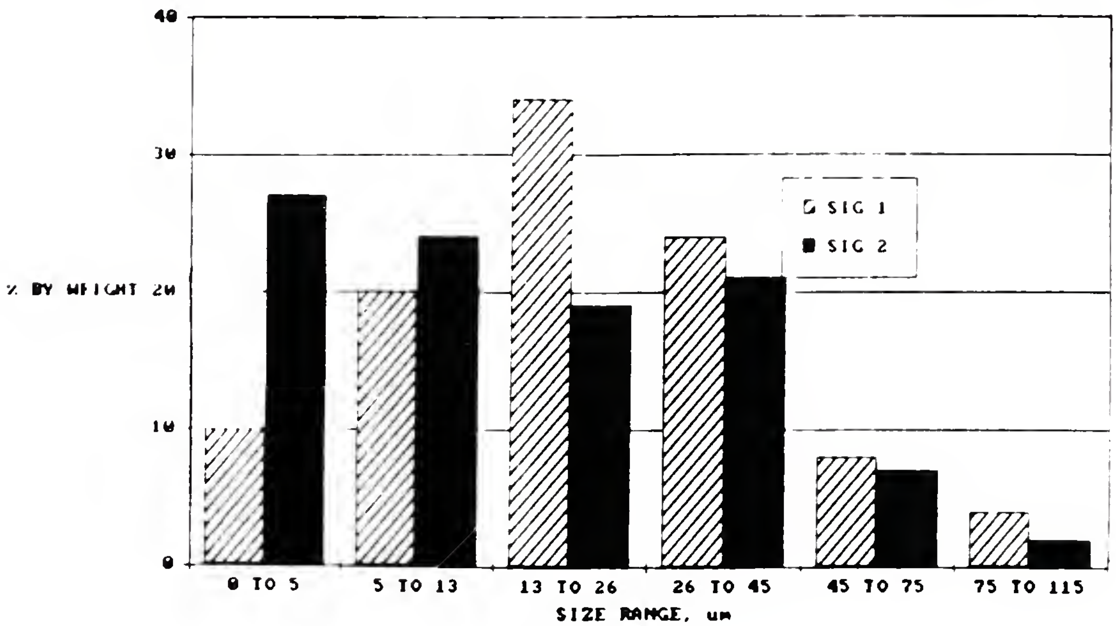
(a) Mean particle size: .... 12 µm

(b) % > No. 325 sieve (45 µ)................. 9 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

The values recorded for this fly ash of a 12 μm mean size and only 9% greater than 45 μm indicate a fly ash somewhat finer than the "typical"

SIG-1 ash that is the basis for comparison. As indicated in the bar charts, this ash is generally similar to SIG-1 in the coarser size ranges, but lacks some of the medium-sized 13 to 26 μm sized material and is much richer in the finest size range, below 5 μm.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g:.................. 2.1

Surface area as measured by high pressure mercury penetration, m^2/g:.................................. 4.8

Blaine fineness, cm^2/g:............................3200.

Blaine fineness after ignition at 750°C, cm^2/g......2200.

(b) Interpretation of surface area values

Despite the finer particle size characteristics of this ash as compared to SIG-1, the surface area values recorded by water vapor and mercury penetration methods are both much lower than that of SIG-1; the water vapor area is only 60% of that for SIG-1 and the mercury penetration value only about one third of it. Perhaps this discrepancy is associated with the lack of residual carbon in the present fly ash. In contrast to these results, the Blaine fineness of this fly ash is actually a little higher than that of the SIG-1 ash, which is what one might expect from the finer particle size.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene........ 2.67

Specific gravity as measured by high pressure mercury penetration............................... 2.61

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.27

Specific gravity by gas displacement, using helium pycnometry............................... 2.76

(b) Interpretation:

The present fly ash appears to be rather denser than the common run of Class F fly ashes, the measurements (except for the low nitrogen gas measurement) trending around 2.7. The implication is that the particles should be mostly solid.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash had the second highest content of magnetic particles recorded in these studies, just under 30% by weight. This is somewhat in excess of its content of iron oxide, which is 24%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The major crystalline components detected were quartz (SiO_2), hematite (Fe_2O_3), and magnetite (Fe_3O_4). There is some mullite ($3Al_2O_3 \cdot 2SiO_2$) present, and very surprisingly for a fly ash of such a low analytical CaO content (2.6%), a little crystalline CaO.

(b) Glass: The glass band in this fly ash is fairly intense, and is centered around 24° 2Θ (Cu radiation).

(c) Separated magnetic particles: The crystalline components found in the x-ray diffraction pattern of the magnetically-separated portion of the fly ash were magnetite (Fe_3O_4), hematite (Fe_2O_3), maghemite (Fe_2O_3), and a trace of quartz. There was absolutely no indication of a glass band in this x-ray pattern, in complete contrast to that of the total fly ash from which it was separated.

Scanning Electron Micrographs

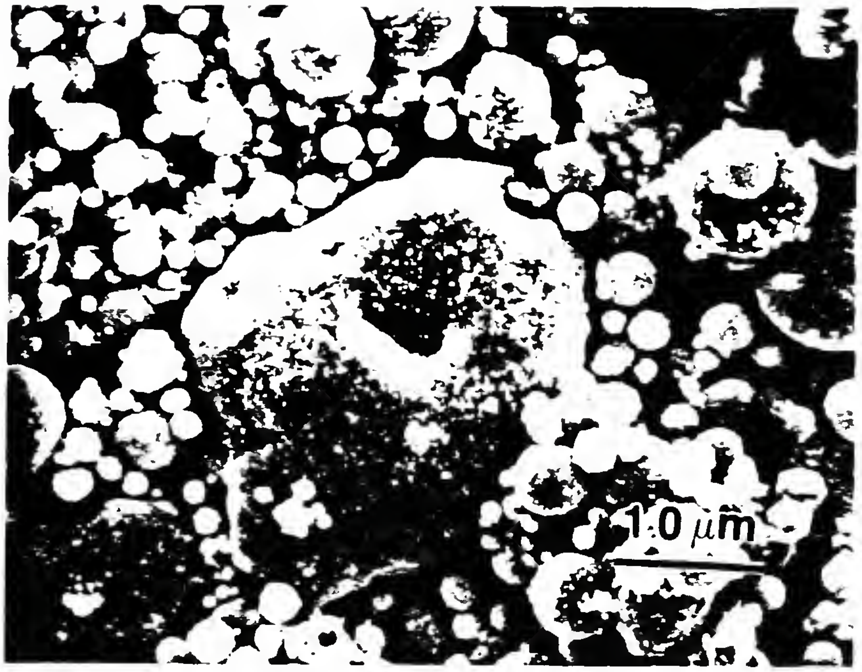
The six micrographs discussed below were selected as representative of the larger set taken in this work.

SIG 2 - A. This micrograph shows something of the fairly extensive numbers of fly ash spheres of the finer size range (below 5 μm) as indicated in the size distribution information above. There are also some larger spheres and one very large moderately rounded grain.

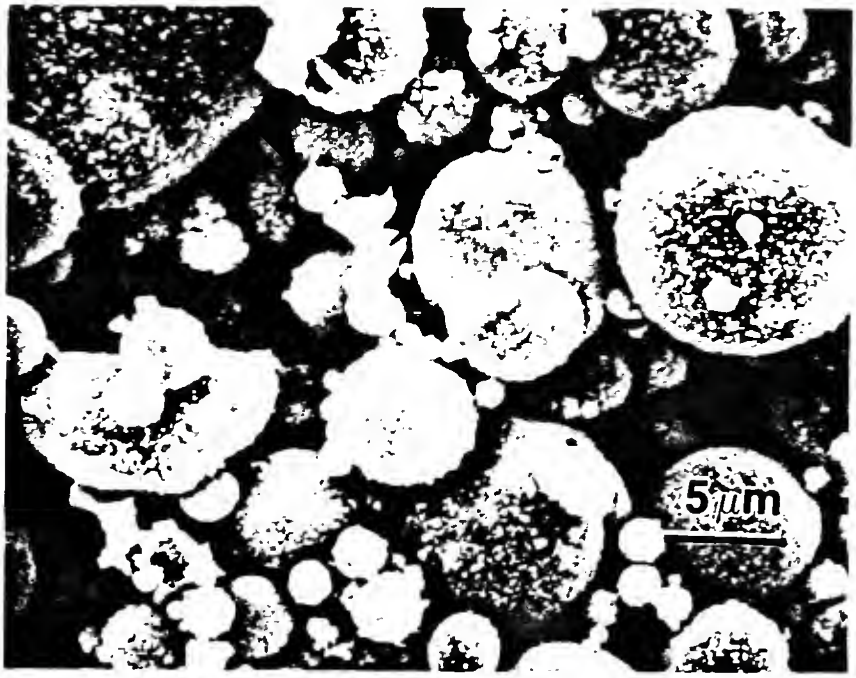
SIG 2 - B. Another area, showing more of the intermediate size range of spheres. There seems to be a heavy coating or deposit roughening up the surface of all of the particles.

SIG 2 - C. Despite the low carbon content, a few detectable carbon coal relicts are identifiable here and there in the fly ash. Several distinct carbon-bearing grains are seen here, including the long complex grain in the bottom of the figure and the bright, sharp-edged fragment in the upper right quadrant.

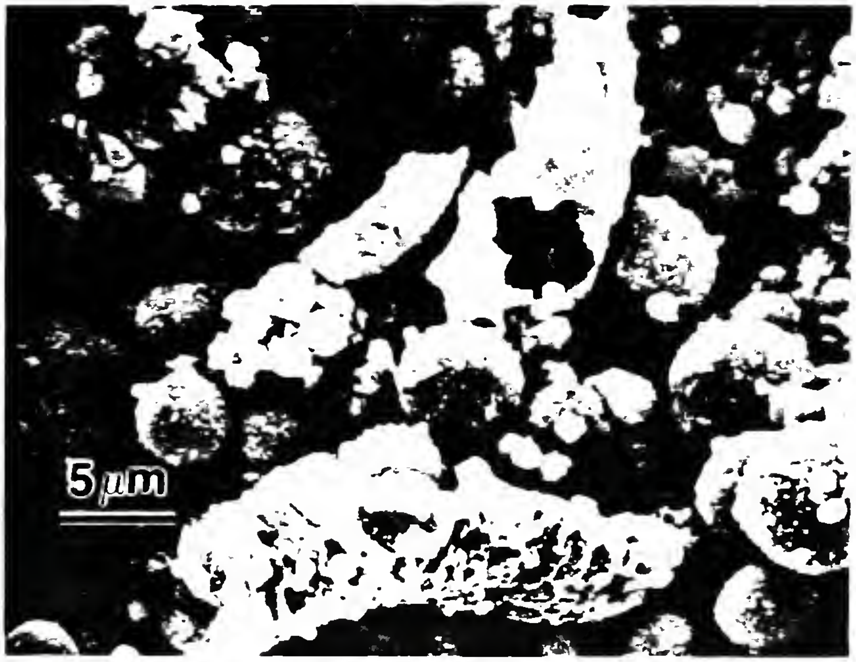
SIG 2 - D Another large carbon grain, shaped somewhat like a lamb chop, occupies the middle part of this figure. One feature noted here of some importance is that the seeming deposition of material on the surface of the



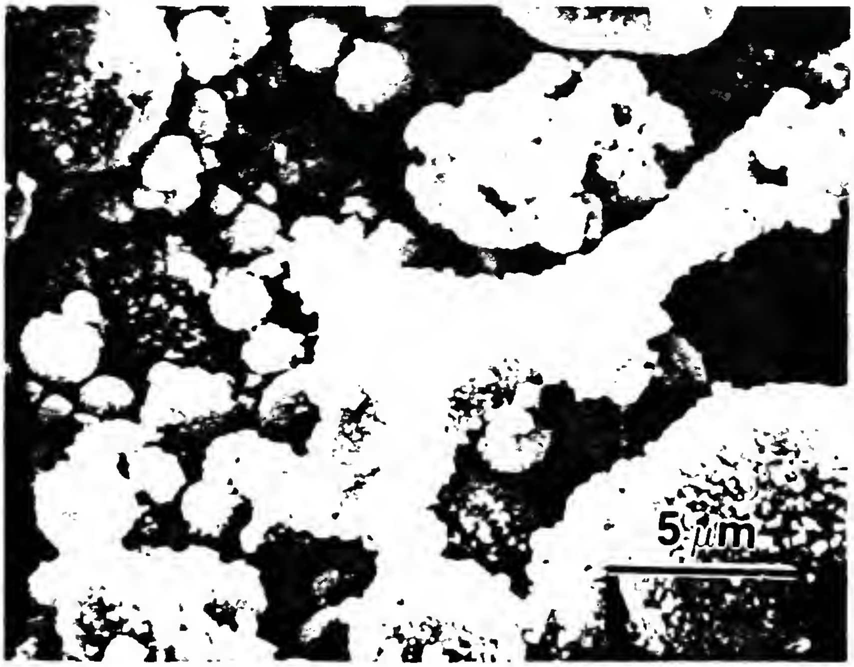
SIG 2 - A Magnification: 2000x.



SIG 2 - B Magnification: 3000x.



SIG 2 - C Magnification: 3000x.



SIG 2 - D Magnification: 5000x.

spheres is also present on the surface of this particle. This suggests that it may have been formed by a condensation process of some material vaporized from the solid in the hottest part of the boiler and then condensed on all the particles present.

SIG 2 - E An attempt was made to study this material by examining the presumed surface deposit at high magnification. This figure shows a 7 μm sphere taken at 10,000 x to try to elecidate the deposit structure. Not much information could be gained.

SIG 2 - F One test that was carried out was an attempt to see if the presumed coating is soluble. A portion of the fly ash was shaken for 10 minutes in excess water in the standard test for soluble alkalies, then filtered, and finally washed with excess water. This micrograph shows the appearance of a representative area after this treatment. It is obvious from this that the presumed coating material is not water soluble.

(2) Interpretation

This fly ash appears to be mostly made up of spherical particles that are probably almost entirely solid, although a few particles of detectable carbon residue is observed here and there. The fly ash is distinguished among by a heavy apparent coating or surface roughness, which seems to be a deposit on carbon grains as well as fly ash spheres. The coating or surface material is not removable by washing in water.

Results of Pozzanic Index Test With Cement

This fly ash gave reasonably adequate results in the pozzolanic index tests with Cement "A". In the standard test, despite a slight decrease in the water demand the strength developed was only 66% of that of the reference cement mortar. However in the modified test

SIG 2 - E Magnification: 10000x.

SIG 2 - F Magnification: 7000x.

carried out at a straight 30% weight replacement and no adjustment of water content, the strength developed reached 87 percent of the control, a quite respectable figure.

Summary Characterization

This fly ash seems to be a perfectly typical Class F fly ash in terms of its chemistry. It has a relatively high iron content and about 30% of the particles are magnetic, which is rather undesirable. Nevertheless the size distribution is reasonably fine, and the surface area more or less normal. The particles seem to have acquired an insoluble surface deposit of some kind. There is little residual carbon. The standard pozzolanic index test result is somewhat disappointing, but the modified test yielded a good response, and it appears that this should be a reasonably adequate fly ash for most purposes.

Fly Ash No. 11: RPL-1

Richmond Station, Richmond Power and Light Department
Wayne County, IN (Central Indiana)

Introduction

This fly ash was sampled from the silo serving both Units 1 and 2 of this small (100 MW) municipal utility station located at the eastern edge of Central Indiana. The plant burns mostly Indiana bituminous coal but about 20% of the coal burned is bituminous coal from Kentucky. The station operates as a base load facility. The Class F fly ash produced is marketed commercially through a national fly ash broker.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 10YR 5/1. The verbal equivalent is "gray".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	2.48
% SiO_2	42.8
% Al_2O_3	29.1
% Fe_2O_3	18.4
% Na_2O	0.13
% K_2O	1.85
% SO_3	0.04
% MgO	1.92
% P_2O_5	1.20
% TiO_2	1.23
Total	99.2

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3...............90.3
Total alkalies, as equivalent % Na_2O.......... 1.35

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 5.50
% carbon by LECO analysis, ignited wt. basis...4.62

The following are determined on an oven-dry basis:

% Total SO_3 ....0.69
% Soluble SO_3.................................0.44
Percentage of the total SO_3 that is soluble.... 64%

% Soluble Na_2O............................... 0.03
% Soluble K_2O................................ 0.01
% Total alkalies, as equiv. % Na_2O.............1.28
% Soluble alkalies, as equivalent % Na_2O...... 0.03
Percentage of the alkalies that are soluble:.... 2%

(4) Chemical analysis interpretations

Again, this fly ash is of a typical Class F composition, with total SiO_2 + Al_2O_3 + Fe_2O_3 content again 90 %. This includes a moderate iron content of about 18% Fe_2O_3. The CaO content is again about 2-1/2 %, alkali content at less than 1-1/2 % is modest, and this time the sulfate content is even more modest. The residual carbon here is however appreciable, with a loss on ignition of over 5%.

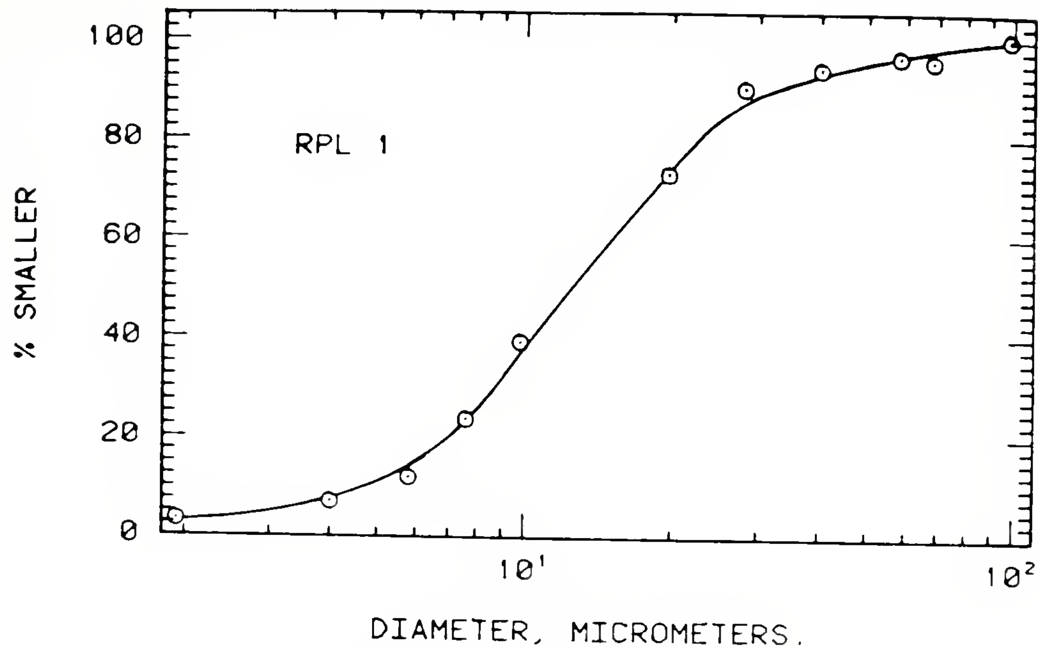
Physical Characteristics

(1) Particle size parameters

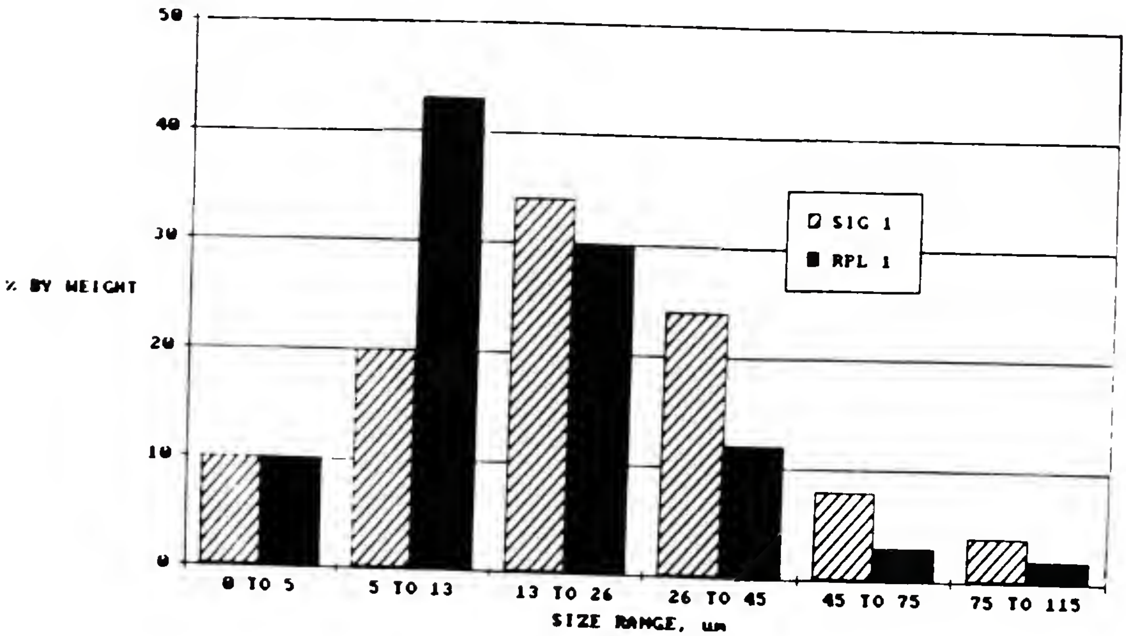
(a) Mean particle size: .... 12 µm

(b) % > No. 325 sieve (45 µ)................. 5 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

The values recorded for this fly ash of a 12 μm mean size and only 5% greater than 45 μm represent another fairly fine fly ash. As indicated in

the bar chart, the coarser sizes are rather under-represented as compared with the "typical" SIG-1 ash; in contrast the content of particles in the 5 to 13 μm size fraction is about twice as great.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................. 6.9

Surface area as measured by high pressure mercury penetration, m^2/g:.................................. 9.2

Blaine fineness, cm^2/g:...........................2800.

Blaine fineness after ignition at 750° C, cm^2/g.....2900.

(b) Interpretation of surface area values

Both types of surface area measurements record fairly high surface areas for this fly ash, about 7 and about 9 m^2/g respectively. This is rather higher than even the fineness of the size distribution would indicate. The Blaine fineness is moderate, only about 2800 cm^2/g, and is unchanged by removing the residual carbon by ignition.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene......... 2.40

Specific gravity as measured by high pressure mercury penetration.................................. 2.46

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.27

Specific gravity by gas displacement, using helium pycnometry................................ 2.74

(b) Interpretation:

The specific gravity measurements for this fly ash are generally in the vicinity of 2.4 (except for the helium gas displacement, which is higher), and suggest the presence of appreciable contents of hollow spheres in this material.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash had about the average content of magnetic particles, the percentage determined being 23.2%. This is somewhat in excess of the iron oxide content of 18%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash discloses the presence of substantial amounts of quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$), and lesser amounts of magnetite (Fe_3O_4) and hematite (Fe_2O_3). The crystalline peaks are unusually sharp.

(b) Glass: There was only a comparatively weak expression of a glass band detected in the x-ray diffraction pattern of this fly ash. This was centered at about 23° 2Θ, the tridymite-type silica glass position.

(c) Separated magnetic particles: The crystalline components found in the x-ray diffraction pattern of the magnetically-separated portion of the fly ash were magnetite(Fe_3O_4), hematite (Fe_2O_3), maghemite (Fe_2O_3), and traces of quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$).

Scanning Electron Micrographs

The following four micrographs were chosen as representative of the

larger set taken of this fly ash.

(1) Descriptions of Micrographs

RPL 1 - A. A fairly typical field for this fly ash, showing the expected large proportion of particles in the roughly 10 μm size range. While many are spheres, quite a few are not. There are a number of incompletely rounded inorganic particles, and especially in the top half, a number of carbon fragments or carbon fragments with very fine spheres still attached.

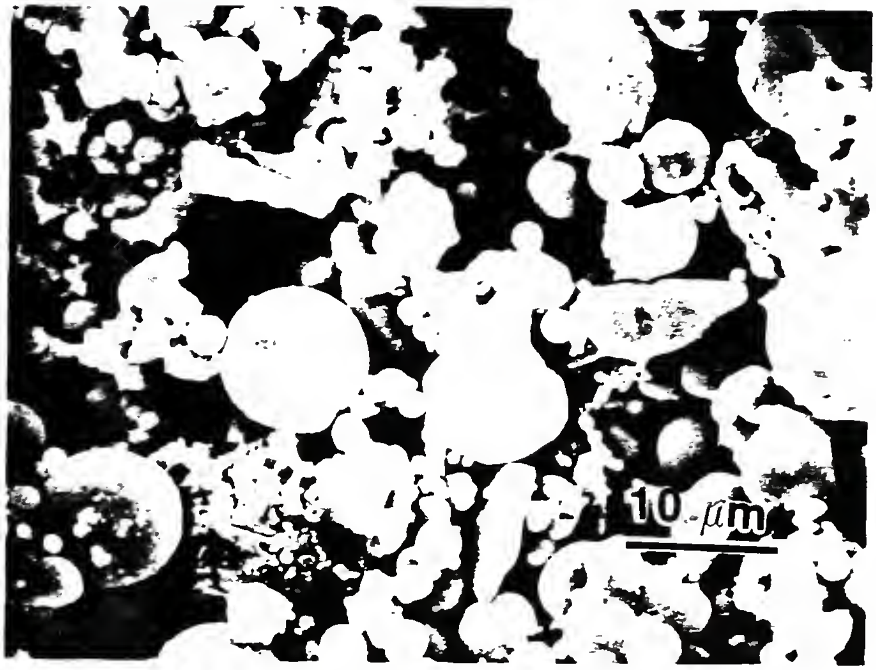
RPL 1 - B. Another area, showing similar particles. The spheres in this fly ash are completely free of any form of deposit, which may correlate with its very low sulfate content. There is a large carbon flake in the upper left corner, and a residual cluster of very fine spheres held together presumably by a thin carbon residue. Another such cluster occurs in the lower right corner.

RPL 1 - C. The presence of unburned carbon is more prominent in this area. The large flake in the center of the figure is unmistakable. There are a substantial number of carbon-bound clusters of the order of 20 to 30 μm in size scattered over the field.

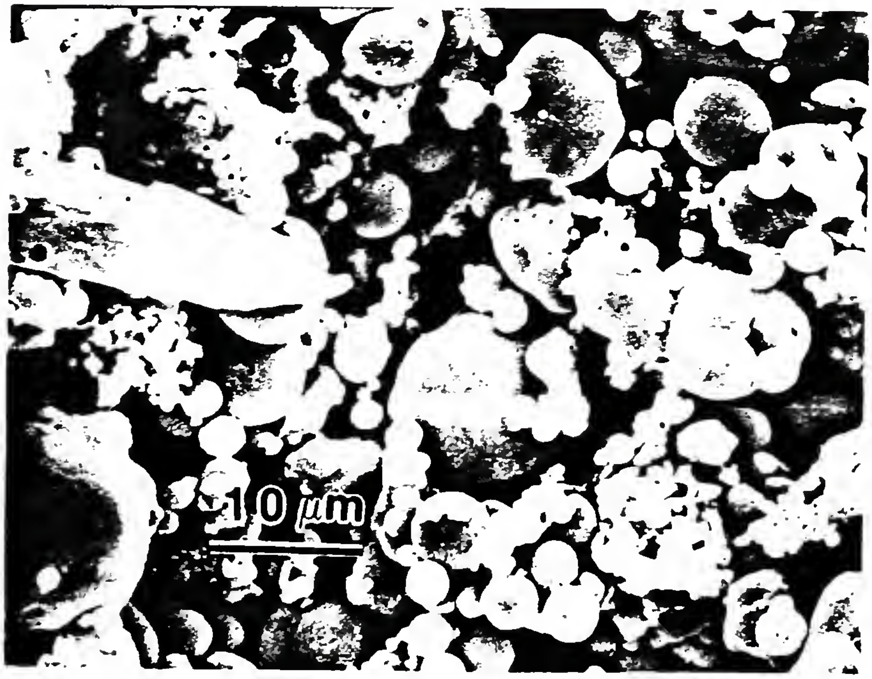
RPL 1 - D Another micrograph showing the general range of particle sizes in this fly ash. The large imperfectly rounded grain just below the center, and a similar but smaller grain just below the scale marker show indications of being hollow. There is a very large, mostly carbon grain taking up most of the upper right hand quadrant of this micrograph.

(2) Interpretation

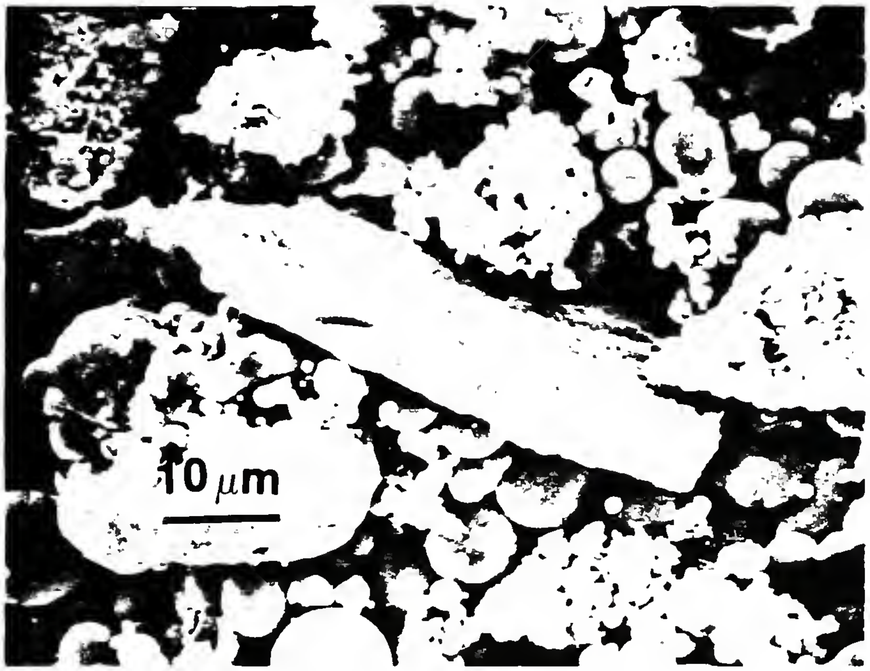
This fly ash contains spherical particles that are entirely smooth in surface texture, with no hint of deposition of material on them. The size ranges are about as expected from the particle size distribution bar plot.



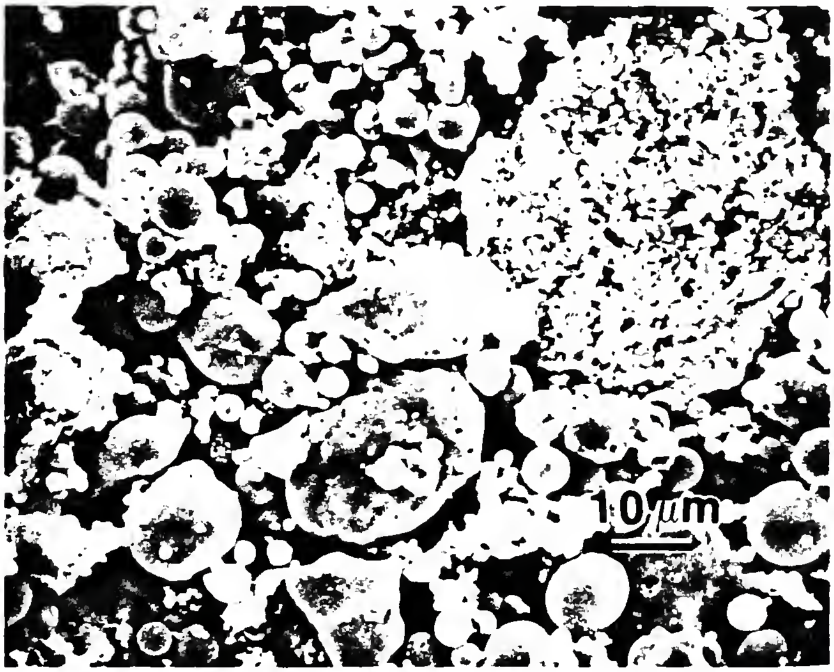
RPL 1 - A Magnification: 2000x.



RPL 1 - B Magnification: 2000x.



RPL 1 - C Magnification: 1500x.



RPL 1 - D Magnification: 1000x.

There are a variety of carbon particles, cluster grains containing carbon supporting and encasing fine inorganic spheres, and large imperfectly rounded spheres, some of the latter being partly hollow.

Results of Pozzolanic Index Test With Cement

Despite the relatively high content of carbon, and despite the relatively high water demand it conferred (about a 15% increase), this fly ash yielded quite good results in the standard pozzolanic index test. The strength developed (with cement "A") was 83% of the that of the reference mortar. The fly ash did not do so well on the modified test with a straight 30% weight replacement, the strength obtained there being only 67% of that of the reference cement mortar.

Summary Characterization

This fly ash seems to be another reasonably typical Class F fly ash, different in chemical terms only with respect to its unusually low sulfate content. The carbon content is relatively high, and carbon particles show up fairly prominently in the scanning microscope examination. The fly ash does not have a large content of the finest sizes of particles, but it is generally fine and has little oversize material. On balance, it should be an adequate fly ash for most purposes.

Fly Ash No. 12: IME-1

Tanners Creek Station, Indiana and Michigan Electric Co.
Dearborn County IN (Southeast Indiana)

Introduction

This fly ash was sampled directly from a hopper serving the first-field precipitator bank of Unit 2 of this large (1050 MW) generating station along the Ohio River in the extreme southeast corner of the State. The coal burned is a Western bituminous coal, thought to be from Utah. The station is operated as a base load generating station for the IME system. The ash is not marketed commercially.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 10YR 5/1. The verbal equivalent is "gray".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	7.34
% SiO_2	53.4
% Al_2O_3	22.7
% Fe_2O_3	4.11
% Na_2O	0.16
% K_2O	0.61
% SO_3	0.70
% MgO	9.85
% P_2O_5	0.59
% TiO_2	0.53
Total	100.0

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3...............80.2

Total alkalies, as equivalent % Na_2O.......... 0.56

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 5.20
% carbon by LECO analysis, ignited wt. basis...3.94

The following are determined on an oven-dry basis:

% Total SO_3 ....0.66
% Soluble SO_3.................................0.10
Percentage of the total SO_3 that is soluble.... 15%

% Soluble Na_2O............................. 0.002
% Soluble K_2O.............................. 0.002
% Total alkalies, as equiv. % Na_2O.............0.53
% Soluble alkalies, as equivalent % Na_2O...... 0.004
Percentage of the alkalies that are soluble:.... 1%

(4) Chemical analysis interpretations

This fly ash would be classified as a Class F ash according to its composition, with a total SiO_2 + Al_2O_3 + Fe_2O_3 content of 80%, although it has more than 7% CaO. The iron oxide content is extremely low at 4% vs. the usual 20 or 25%. The alkali content is also very low, and entirely insoluble. The sulfate content is low and only slightly soluble. An MgO content of almost 10% makes this a very unusual material chemically. The loss-on-ignition value of 5% is high for a modern base-load plant.

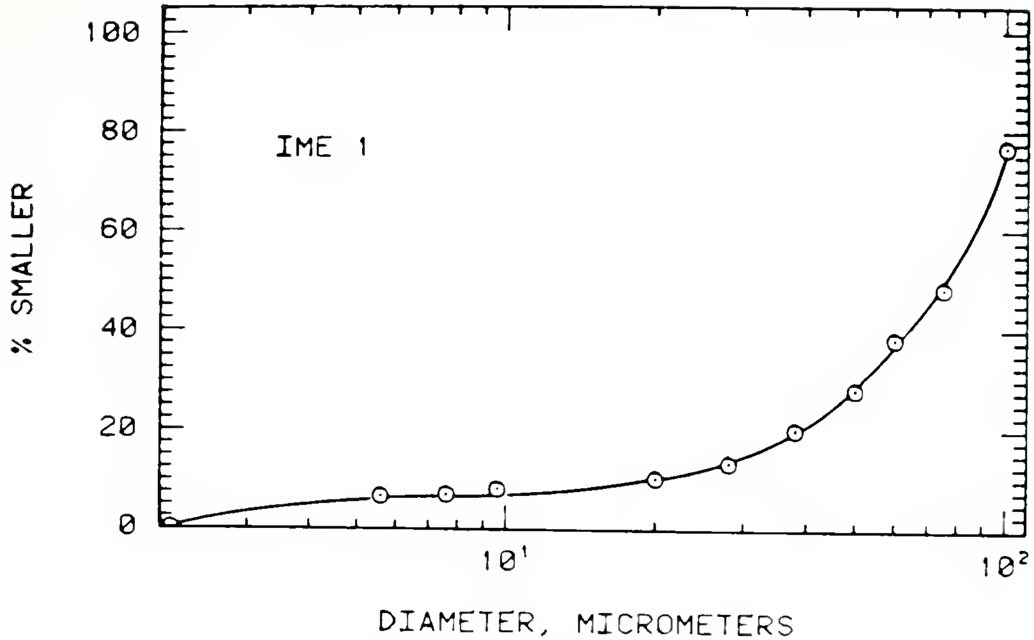
Physical Characteristics

(1) Particle size parameters

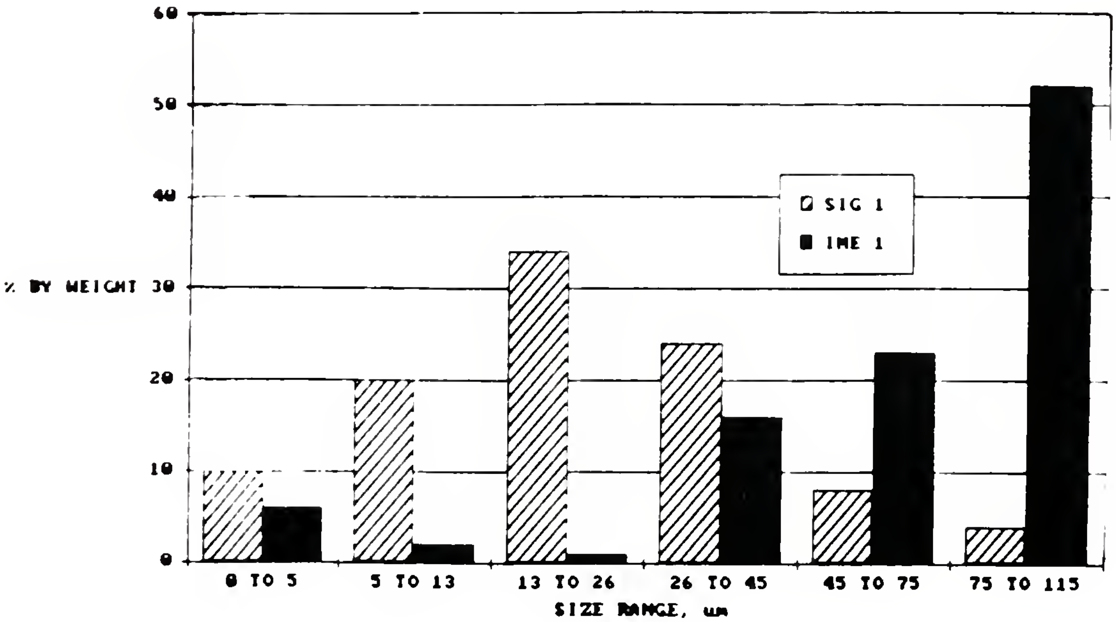
(a) Mean particle size: .... 78 μm

(b) % > No. 325 sieve (45 μm)............... 75 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

This is by far the coarsest fly ash sampled in this project, and indeed the coarsest the writer has ever seen. Only the fact that it

was sampled from a precipitator hopper provides testimony that it is a fly ash at all. The bar graph tells the story rather plainly. While there are particles in all of the size ranges, more than half of the particles by weight are in the coarsest size range, >75 μm.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................. 2.0

Surface area as measured by high pressure mercury penetration, m^2/g:................................. 7.5

Blaine fineness, cm^2/g:........................... 860.

Blaine fineness after ignition at 750° C, cm^2/g..... 820.

(b) Interpretation of surface area values

Both types of surface area measurements record surprisingly high surface areas for this coarse fly ash, but the mercury penetration method is especially and unreasonably high at over 7 m^2/g. The Blaine fineness values are more reasonable, being only about 30 percent or so of that of most fly ashes. The removal of residual carbon by ignition at 750° C makes no apparent difference in this value.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene......... 2.28

Specific gravity as measured by high pressure mercury penetration................................ 2.36

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.28

Specific gravity by gas displacement, using helium pycnometry................................ 2.54

(b) Interpretation:

The specific gravity measurements for this fly ash are generally in the vicinity of 2.3 (except for the helium gas displacement, which is higher). This is almost the lowest value recorded. The low iron oxide content at only 4% undoubtedly contributes to this low value, but the presence of appreciable contents of hollow particles would not be surprising.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash had a content of magnetic particles of 6.1%, more or less in accord with its very low iron oxide content.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash indicated that quartz (SiO_2) was by far the major component, accompanied by traces of mullite ($3Al_2O_3 \cdot 2SiO_2$), of free crystalline CaO, and possibly of periclase (MgO). The quartz peaks are unusually strong and sharp and the quartz present is obviously well crystallized.

(b) Glass: There was a moderate intensity, symmetrical glass band present with a maximum near 24° 2Θ (Cu radiation). This confirms the tridymite-like structure of the glass despite the relatively high CaO content for a class F fly ash.

(c) Separated magnetic fraction: The x-ray diffraction pattern of the magnetically-separated portion of the fly ash contained quartz (SiO_2) as its major crystalline component, apparently carried in by

attachment to other substances. There were reasonably strong peaks for magnetite (Fe_3O_4), hematite (Fe_2O_3), and maghemite (Fe_2O_3) as well. The existence of a glass band in the pattern is problematical.

Scanning Electron Micrographs

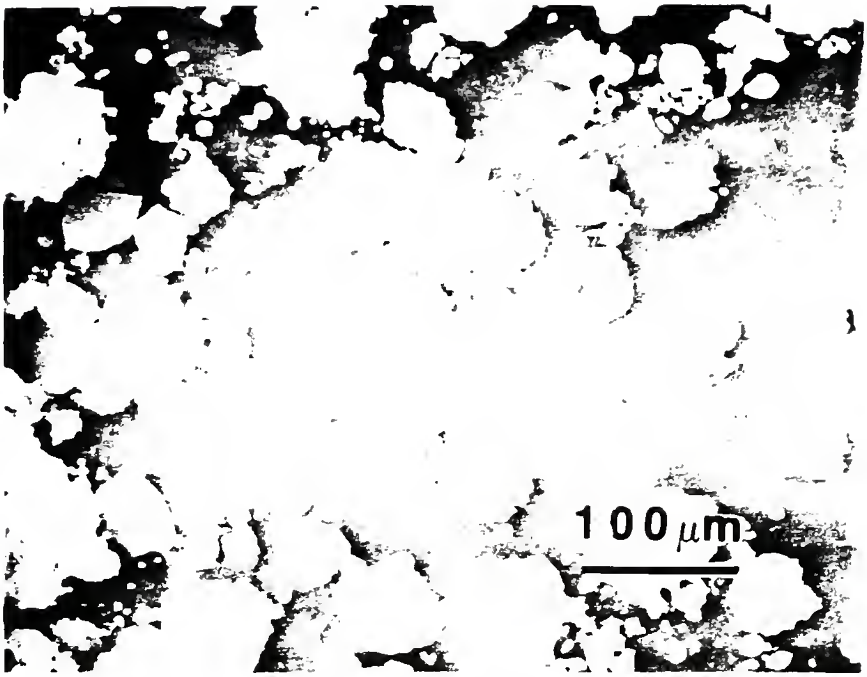
The following four micrographs were chosen as representative of the larger set taken of this fly ash.

(1) Descriptions of Micrographs

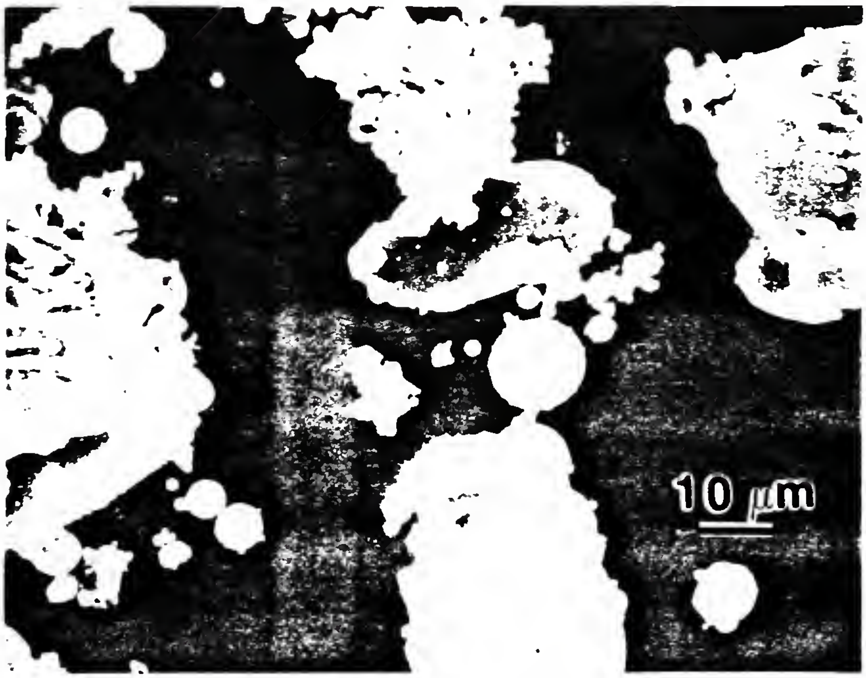
IME 1 - A. An overall idea of the kinds and sizes of particles present in this very coarse material can be secured by examining this micrograph of a typical area. The coarseness of the ash was such that a special tape specimen preparation technique was required for these micrographs, which shows the particles spread out much more than the silver membrane technique used for all other fly ashes. It can be seen that only a few of the particles are spheres; most are clusters or very slightly rounded large grains.

IME 1 - B. It is possible to see some of the individual grains clearly in this micrograph. There are a few spheres, mostly in the 10 μm or finer sizes. There are some imperfectly rounded coarse grains, such as the elongated grain above the sphere in the center and the grain at the top right. Most of the rest of the particles are cluster grains such as the 30 μm grain at the top center, or the even larger one at the left.

IME 1 - C. The surface texture of the individual spheres varies a bit from sphere to sphere, but as seen here, it is relatively smooth for most spheres. The grainy structure in the surface of the large sphere



IME 1 - A Magnification: 200x.



IME 1 - B Magnification: 1000x.

IME 1 - C Magnification: 700x.

IME 1 - D Magnification: 1000x.

at the left is probably due to layers of mullite crystals just below the surface.

IME 1 - D An idea of the nature of the very large complex grains is provided in this micrograph. Note that this "slaggy" overall particle is mostly rounded and partly hollow, and it contains a large number of smaller perfect spheres within it.

(2) Interpretation

The unusually coarse nature of this fly ash and the overwhelming proportion of grains like that of IMC 1 - D is only explainable on the basis that either the boiler had no economizer unit ahead of the fly ash precipitator (which would be most unusual), or more likely the economizer unit was being bypassed, and coarse material which ordinarily would not have reached the precipitators was being removed at the first field precipitators along with the "proper" fly ash.

Results of Pozzolanic Index Test With Cement

As might have been expected, the results of the pozzolanic index tests on this very coarse ash were entirely unsatisfactory. The water demand was excessive, requiring more than 30% of additional water to meet the prescribed flow, and the strength developed in the standard test with cement "A" was only 12% of that of the reference cement mortar. The result obtained in the supplementary test in which no adjustment for water demand was not much better, the strength being 17% of that of the reference cement mortar.

Summary Characterization

It is evident that this "fly ash" is indeed so heavily contaminated with economizer ash as to be entirely unusable in concrete. The reader should be cautioned that the sample secured and tested here, while taken with the approval and under the practical direction of plant personnel, may very well not be representative of the normal output of this power station.

Fly Ash No. 13: CPC-1

Campbell Station, Consumer Power Co.
Ottawa County, MI (Southwest Michigan)

Introduction

This fly ash was a sample provided from this large (700 MW) generating station in the southwestern part of Michigan by a fly ash broker who regularly sells the ash for use in northeastern Indiana as well as in Michigan. There are essentially no local sources of fly ash in this northeastern Indiana, because of the way the power grid has evolved.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 5/2. The verbal equivalent is "olive gray".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	1.60
% SiO_2	46.6
% Al_2O_3	23.3
% Fe_2O_3	19.5
% Na_2O	0.49
% K_2O	2.69
% SO_3	0.14
% MgO	3.54
% P_2O_5	1.20
% TiO_2	1.44
Total	100.5

(2) Parameters derived from above analyses

Total % of $SiO_2 + Al_2O_3 + Fe_2O_3$...............80.2

Total alkalies, as equivalent % Na_2O.......... 0.56

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 5.20
% carbon by LECO analysis, ignited wt. basis...3.94

The following are determined on an oven-dry basis:

% Total SO_3 ....0.66
% Soluble SO_3.................................0.10
Percentage of the total SO_3 that is soluble.... 15%

% Soluble Na_2O.............................. 0.002
% Soluble K_2O............................... 0.002
% Total alkalies, as equiv. % Na_2O.............0.53
% Soluble alkalies, as equivalent % Na_2O...... 0.004
Percentage of the alkalies that are soluble:.... 1%

(4) Chemical analysis interpretations

This fly ash would be classified as a Class F ash according to its composition, with a total $SiO_2 + Al_2O_3 + Fe_2O_3$ content of 80%, although it has more than 7% CaO. The iron oxide content is extremely low at 4% vs. the usual 20 or 25%. The alkali content is also very low, and entirely insoluble. The sulfate content is low and only slightly soluble. An MgO content of almost 10% makes this a very unusual material chemically. The loss-on-ignition value of 5% is high for a modern base-load plant.

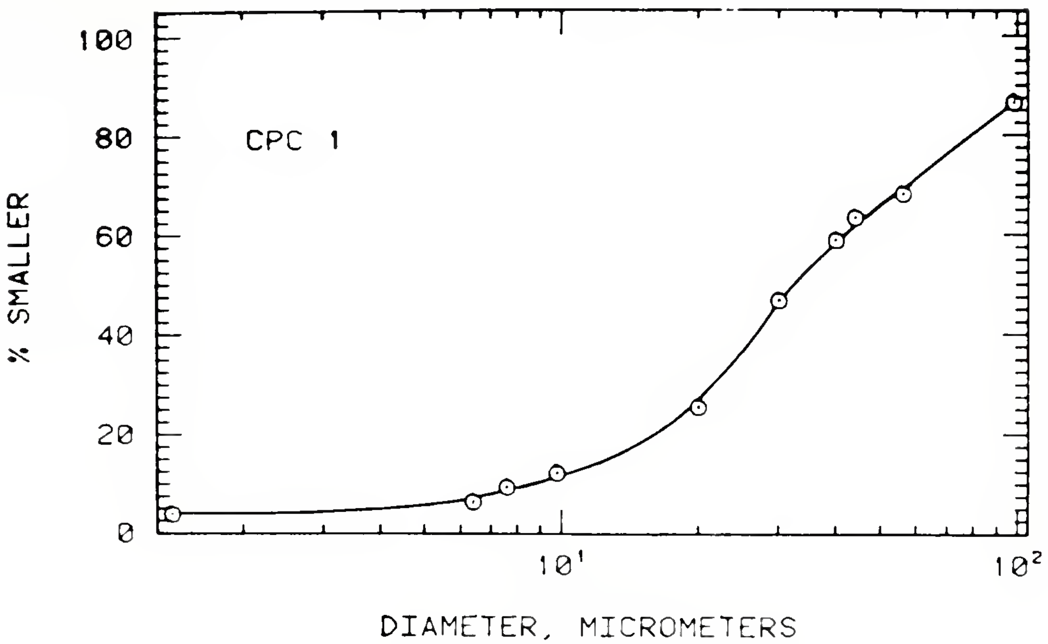
Physical Characteristics

(1) Particle size parameters

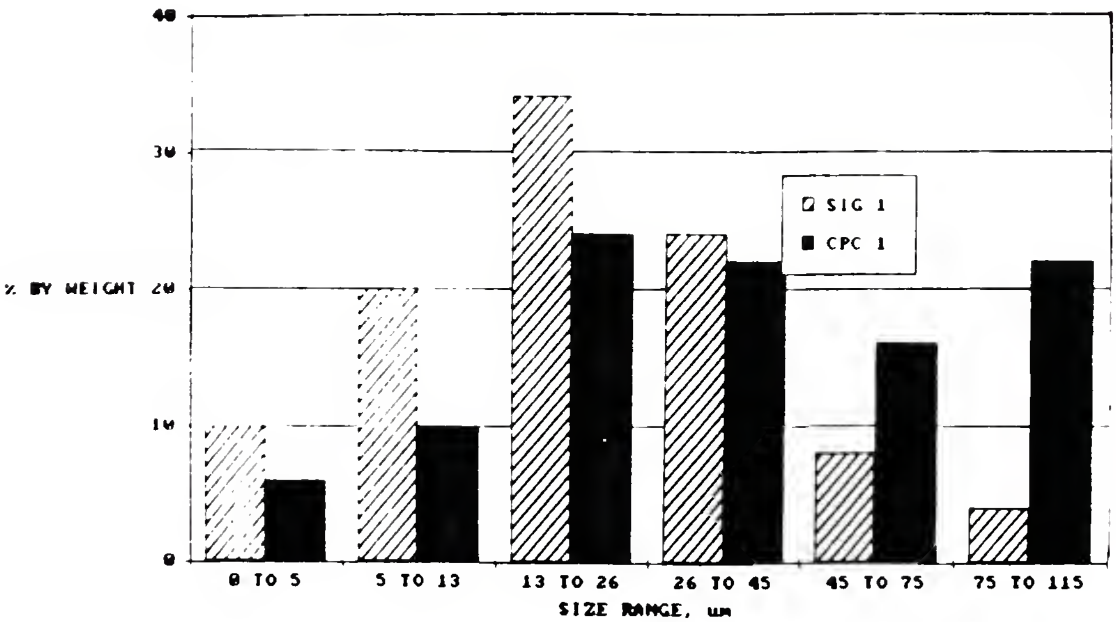
(a) Mean particle size: .... 78 µm

(b) % > No. 325 sieve (45 µm)................ 75 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

This is a relatively coarse fly ash, as indicated by the high value for the mean particle size (32μm) and the relatively high content of

oversize particles (38%). Examination of the size distribution bar chart shows that the contents of the three finer size categories are lower than the comparable contents for the "typical" SIG-1 ash, and the two coarsest categories are over-represented. The very large content of particles >75 µm is especially noteworthy.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................. 2.1

Surface area as measured by high pressure mercury penetration, m^2/g:.................................. 9.6

Blaine fineness, cm^2/g:.......................... 1400.

Blaine fineness after ignition at 750° C, cm^2/g.... 1500.

(b) Interpretation of surface area values

Both types of surface area measurements again record surprisingly high surface areas for this coarse fly ash; again the mercury penetration result is unreasonably high at almost 10 m^2/g. The Blaine fineness values are again more reasonable, the 1400 m^2/g value being appropriate for a coarse but not unreasonably coarse fly ash.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene......... 2.27

Specific gravity as measured by high pressure mercury penetration.................................. 2.45

Specific gravity by gas displacement, using nitrogen gas pycnometry.......................... 2.25

Specific gravity by gas displacement, using helium pycnometry................................ 2.58

(b) Interpretation:

The specific gravity measurements for this fly ash are similar to those found in the previous IME-1 fly ash, being again more or less in the vicinity of 2.3 (except for the helium gas displacement, which is again higher). This is a quite low value, especially in view of the reasonably high iron oxide content in the present ash. Thus the presence of appreciable contents of hollow particles would again be likely.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash had a content of magnetic particles of 23.8%, more or less commensurate with its iron oxide content of about 20%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash indicated the presence of a rather smaller content of quartz (SiO_2) than is usually found. This is accompanied by a substantial amount of mullite ($3Al_2O_3 \cdot 2SiO_2$), and lesser contents of magnetite (Fe_3O_4) and hematite (Fe_2O_3).

(b) Glass: There was a strong glass band observed for this fly ash, with its maximum at 23° 2Θ (Cu radiation), confirming the tridymite-like structure of the glass.

(c) Separated magnetic fraction: The x-ray diffraction pattern of the magnetically-separated portion of the fly ash contained magnetite (Fe_3O_4) and hematite (Fe_2O_3) as its major components, along with traces of of quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$). There was a reasonable

indication of a glass band.

Scanning Electron Micrographs

The following four micrographs were chosen as representative of the larger set taken of this fly ash.

(1) Descriptions of Micrographs

CPC 1 - A. An overall idea of the kinds and sizes of particles present in this fly ash is provided in this figure. The coarse grains are of several types; most of the finer grains are smooth-textured spheres.

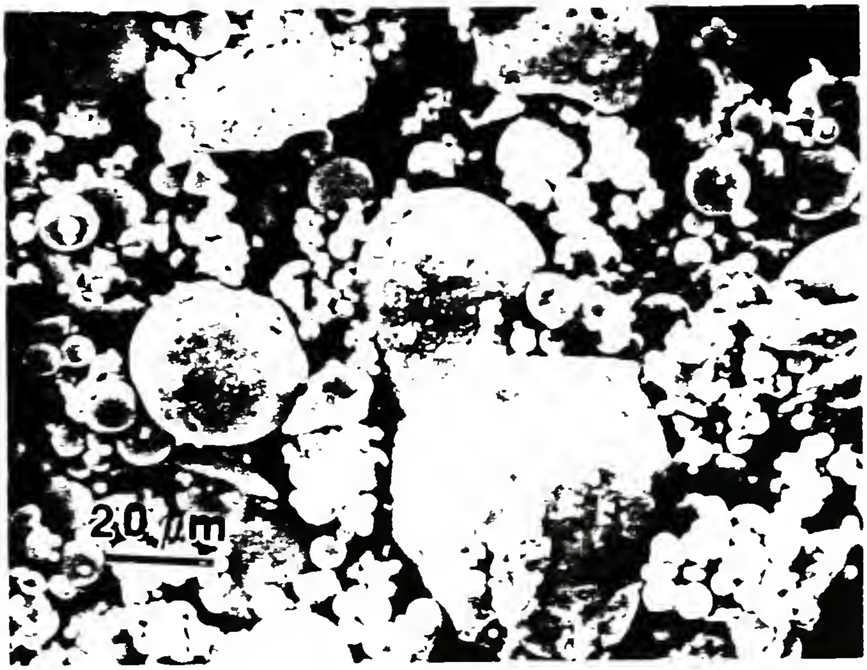
CPC 1 - B. The nature of the finer component can be seen in this micrograph. It is apparent that the spheres are very well formed and perfectly smooth. One or two small residual carbon particles can be seen in the lower right corner.

CPC 1 - C. The fact that not all the particles are spherical can be seen in this micrograph. Note the incompletely rounded grain in the center, the partly-hollow large grain (with vent holes!) under and to the left of the scale bar, and the hollow sphere with smaller spheres apparently coming out

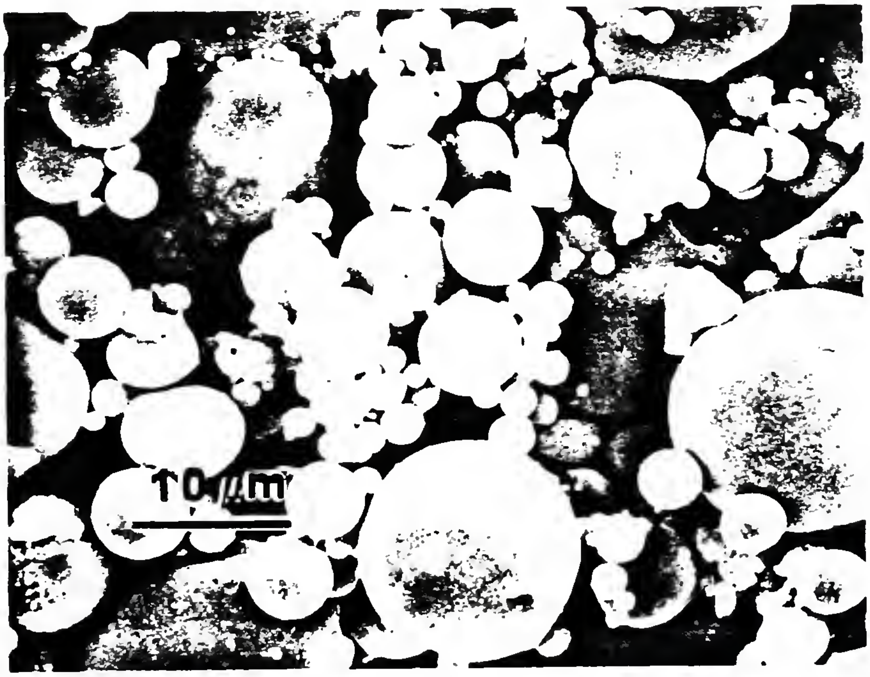
CPC 1 - D An indication that at least some of the particles are hollow is provided by this classical look at a thin-walled plerosphere, with its contents of interior particles of several kinds.

(2) Interpretation

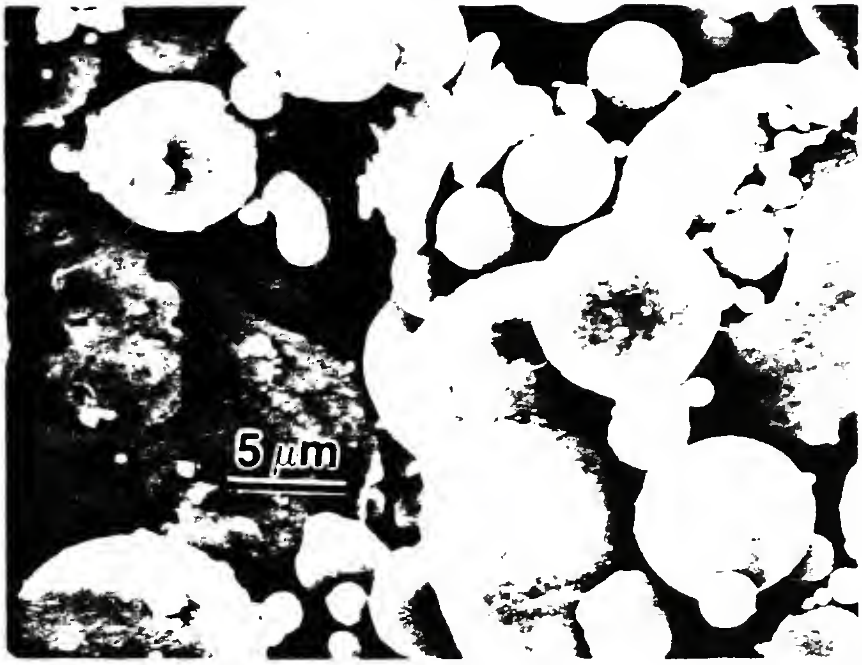
This appears to be a clean, well-fired fly ash with a relatively coarse size distribution, but with a fairly substantial content of fine spherical grains, including hollow ones. Only a minimum of carbon residue is visible, in line with the low carbon content determined by the LECO analysis (1.2%).



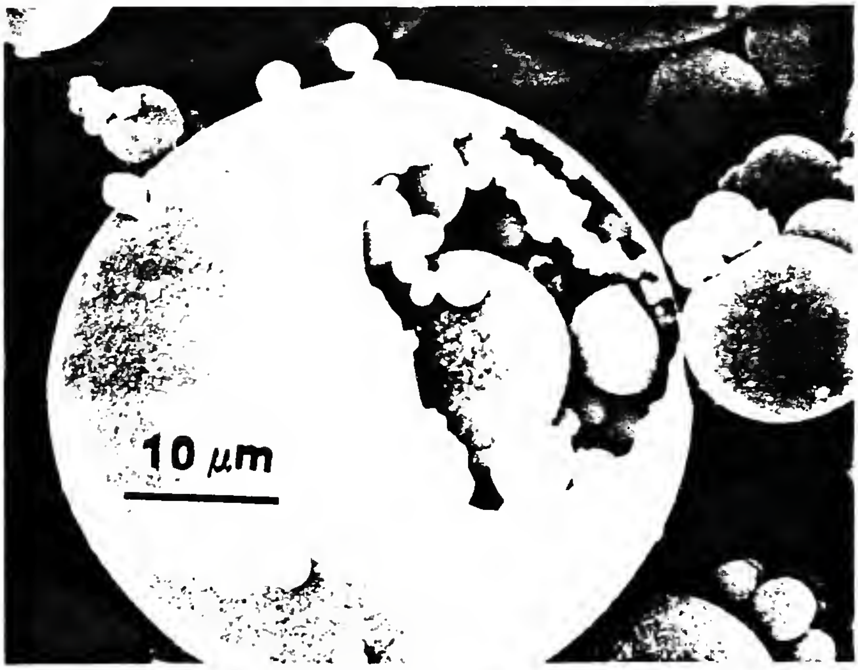
CPC 1 - A Magnification: 700x.



CPC 1 - B Magnification: 2000x.



CPC 1 - C Magnification: 3000x.



CPC 1 - D Magnification: 5000x.

Results of Pozzolanic Index Test With Cement

The results of the pozzolanic index tests on this fly ash are extremely puzzling. Because of the coarse size distribution, one might expect some increase in water demand, and indeed a modest increased water requirement of around 7% was indicated by the testing. However, the standard pozzolanic index test results, incorporating this only modestly higher water content, proved to be very poor. The strengths reached with both cements "A" and "B" were each only 30% of those of their respective cement mortars. The tests on the two cements were carried out entirely separately, with a number of months elapsing between the two sets of trials. On the other hand, both sets of supplementary tests, carried out at a straight 30% weight replacement and no adjustment of water content, gave entirely satisfactory results, the values being 87% for cement "A" and 83% for cement "B". The writer does not have any explanation for this peculiar response.

Summary Characterization

This fly ash appears to be a coarse but otherwise not unusual Class F material, with ordinary class F fly ash chemistry, including a high summation value of the silicon, aluminaum and iron oxides, and relatively low contents of alkalies and sulfate. The finer particles, at least, are clean smooth spheres, and occasional hollow particles are detected. There is very little residual carbon. Yet despite this very ordinary set of characteristics, and an only modest increase in water demand, the standard pozzolanic index test results are very poor. At the same time the straight replacement modified pozzolanic index tests give entirely satisfactory

results, thus introducing an unexplained peculiarity of behavior which has not been resolved.

Fly Ash No. 14: LWL-1

Ericson Station, Lansing Bd. of Water and Light
Ingham County, MI (Southwest Michigan)

Introduction

This fly ash was a sample provided from this medium-sized (200 MW) municipal generating station in southwest of Michigan by a fly ash broker who regularly sells the ash in northeastern Indiana as well as in Michigan. This fly ash, like the previous sample, is imported into northeastern Indiana because of the lack of local sources of fly ash in this portion of the state.

Color

The color of this fly ash in the standard Munsell color system notation is recorded as 5Y 6/1. The verbal equivalent is "light gray".

Chemical Analyses

(1) Total analysis, ignited weight basis

% CaO	1.04
% SiO_2	48.6
% Al_2O_3	33.7
% Fe_2O_3	5.84
% Na_2O	0.62
% K_2O	3.70
% SO_3	0.08
% MgO	2.28
% P_2O_5	0.85
% TiO_2	1.56
Total	98.3

(2) Parameters derived from above analyses

Total % of $SiO_2 + Al_2O_3 + Fe_2O_3$...............88.1

Total alkalies, as equivalent % Na_2O.......... 3.05

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 5.40
% carbon by LECO analysis, ignited wt. basis...4.55

The following are determined on an oven-dry basis:

% Total SO_3 ....0.47
% Soluble SO_3..................................0.30
Percentage of the total SO_3 that is soluble.... 64%

% Soluble Na_2O............................... 0.03
% Soluble K_2O................................ 0.04
% Total alkalies, as equiv. % Na_2O.............2.89
% Soluble alkalies, as equivalent % Na_2O...... 0.06
Percentage of the alkalies that are soluble:.... 2%

(4) Chemical analysis interpretations

This is a Class F fly ash of rather unusual chemical composition, in that while the content of combined $SiO_2 + Al_2O_3 + Fe_2O_3$ is normal at about 88%, the total is made up of far less Fe_2O_3 (6%) and far more Al_2O_3 (34%) than is usual; the usual is something around 20% of the former and 25% of the latter. The alkali content is a bit on the high side (3%) but insoluble; the sulfate content is low (about 1/2% on testing after oven drying) but mostly soluble. The residual carbon level at about 4-1/2% is higher than desirable.

Physical Characteristics

(1) Particle size parameters

(a) Mean particle size: .... 28 µm

(b) % > No. 325 sieve (45 µm)............... 28 %

(2) Parameters derived from above analyses

Total % of SiO_2 + Al_2O_3 + Fe_2O_3...............88.1

Total alkalies, as equivalent % Na_2O.......... 3.05

(3) Other analyses

Loss on ignition, ignited wt. basis.......... 5.40
% carbon by LECO analysis, ignited wt. basis...4.55

The following are determined on an oven-dry basis:

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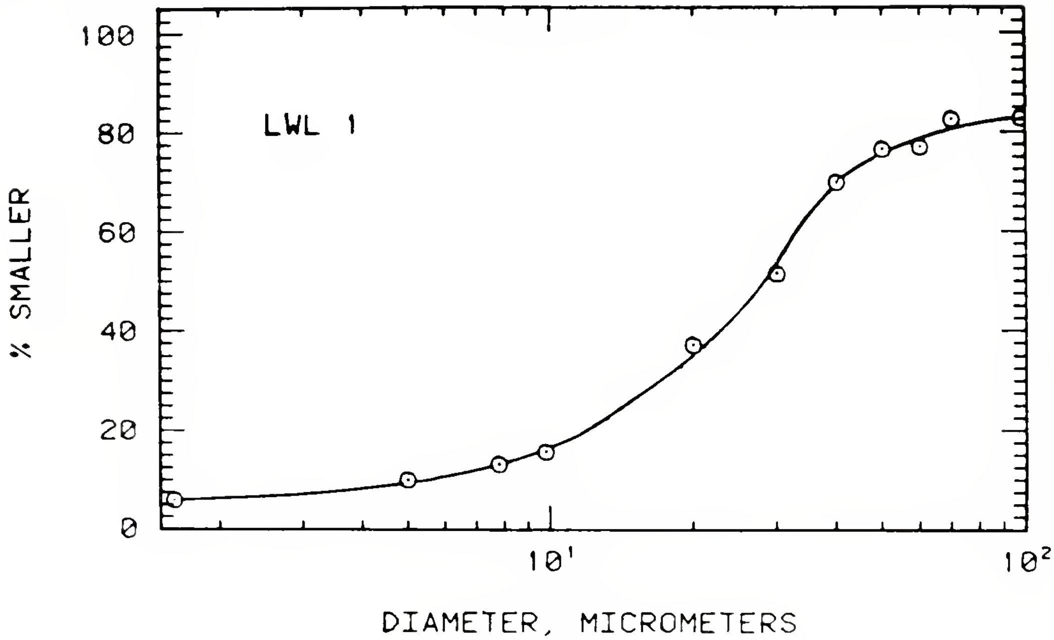
Physical Characteristics

(1) Particle size parameters

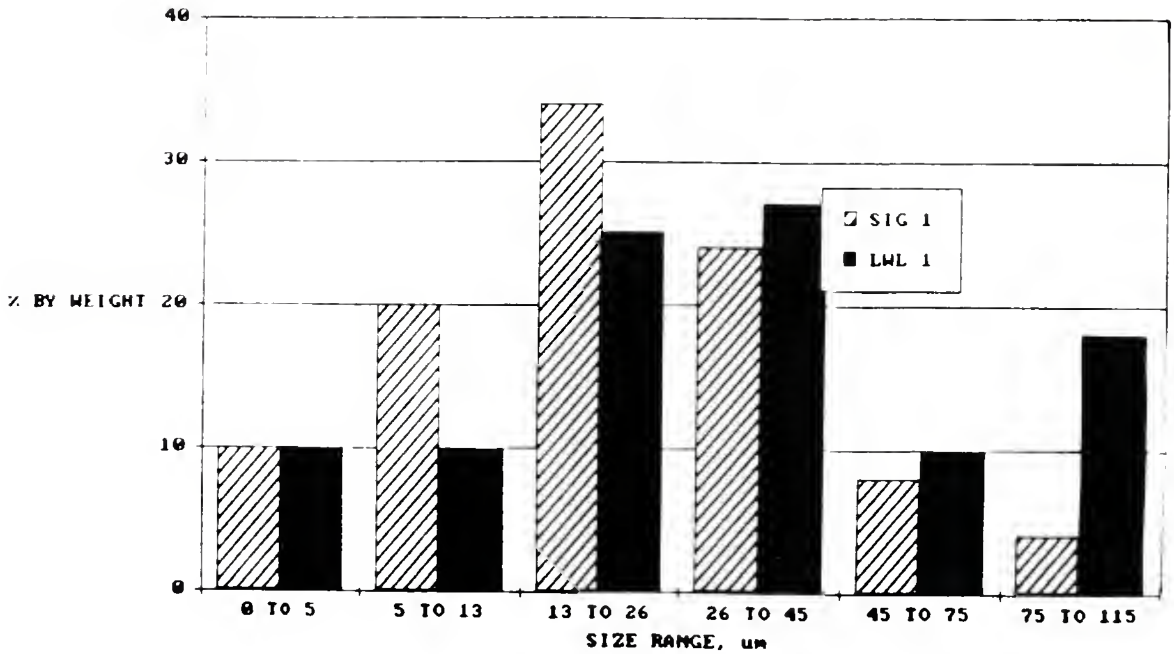
(a) Mean particle size: .... 28 μm

(b) % > No. 325 sieve (45 μm)................ 28 %

(2) Particle size distribution plot



(3) Relative particle size bar plot



(4) Interpretation of particle size distribution

This is also a a relatively coarse fly ash, as indicated by the 28 μm mean particle size and the high percentage of oversize material, almost

30%. The size distribution bar chart shows a deficiency in the intermediate fine categories (5 to 13 μm and 13 to 26 μm sizes), but not in the finest size range, as compared to the SIG-1 "typical" fly ash. There is a substantial content of very coarse (>75 μm) particles.

(5) Surface Area

(a) Measured values:

Surface area to water vapor, m^2/g.................. 2.5

Surface area as measured by high pressure mercury penetration, m^2/g:................................ 9.6

Blaine fineness, cm^2/g:.......................... 2700.

Blaine fineness after ignition at 750° C, cm^2/g.... 2400.

(b) Interpretation of surface area values

Again the surface area measurements, especially the mercury penetration surface area, are higher than could reasonably be expected for a coarse fly ash, the latter again being almost 10 m^2/g. The Blaine fineness values are a bit larger than expected, but not unreasonably so.

(6) Specific Gravity Measurements

(a) Measured values:

Specific gravity by pycnometry in kerosene......... 2.12

Specific gravity as measured by high pressure mercury penetration............................ 2.26

Specific gravity by gas displacement, using nitrogen gas pycnometry......................... 2.11

Specific gravity by gas displacement, using helium pycnometry.............................. 2.38

(b) Interpretation:

The specific gravity measurements for this fly ash are significantly lower than those found in the previous two fly ashes, being around 2.2 or or so, depending on method, rather than a bit over 2.3. The difference is presumably associated with the much lower Fe_2O_3 content in this ash.

Measurements of Physicochemical Parameters

(1) Content of Magnetic Particles

This fly ash had a content of magnetic particles of only 4.4%, a bit lower even than its low Fe_2O_3 content of about 6%.

(2) X-Ray Diffraction Analyses Results

(a) Crystalline components: The x-ray diffraction pattern for this fly ash indicated the presence only of quartz (SiO_2) and a substantial content of mullite ($3Al_2O_3 \cdot 2SiO_2$). No iron-bearing crystalline phases were detected.

(b) Glass: There was a very strong glass band observed for this fly ash, with a maximum again around 23° 2Θ (Cu radiation), confirming the tridymite-like structure of the glass.

(c) Separated magnetic fraction: The x-ray diffraction pattern of the small content of magnetically-separated material of this fly ash surprisingly contained no recognizable peaks for the magnetite, hematite, or maghemite compounds which usually make up the bulk of this material. The pattern showed only strong quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$) peaks with a surprisingly very strong glass band. There was no indication of why the material separated was magnetically responsive.

Scanning Electron Micrographs

The following four micrographs were chosen as representative of the larger set taken of this fly ash.

(1) Descriptions of Micrographs

LWL 1 - A. An illustration of a packed area showing many small and a few larger fly ash spheres and several large cluster grains of residual carbon with embedded small spheres, as is common in this fly ash.

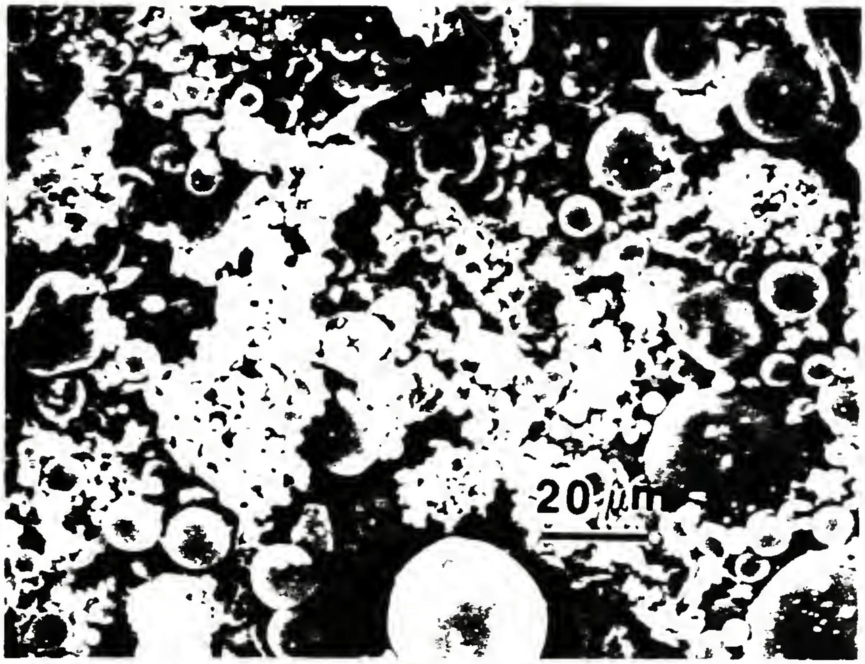
LWL 1 - B. The very smooth surface texture of the spheres of this fly ash show up well in this micrograph, as does the commonness of small residual carbon particles and clusters among the larger inorganic spheres.

LWL 1 - C. An excellent view of one of the large "Swiss cheese" residual carbon grains; the carbon in this grain this has not burned away as much as it has in some grains, where one sees primarily the little spheres sticking together. Here there is mostly carbon, and many of the spheres have dropped out.

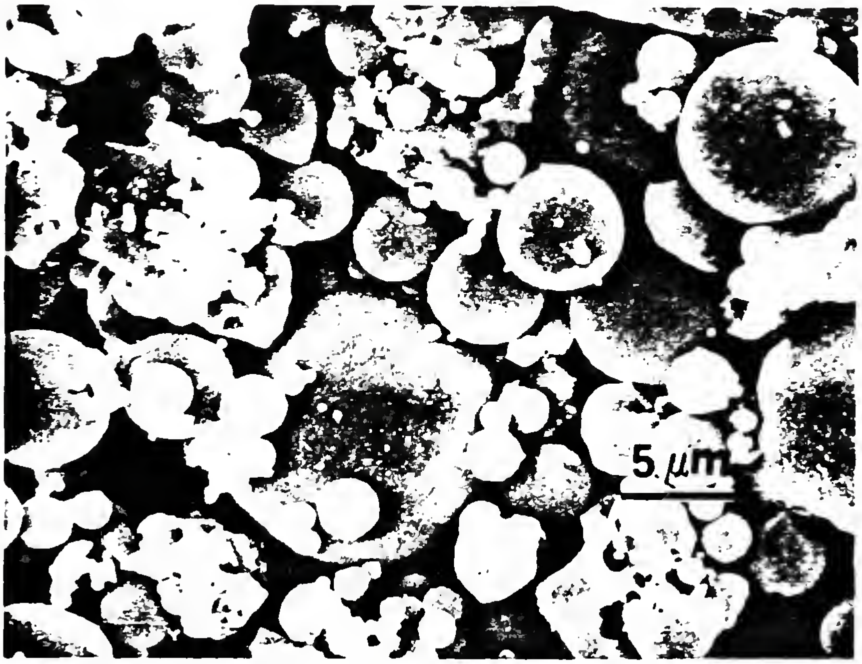
LWL 1 - D An indication that for this fly ash as well, at least some of the spheres are hollow. Also note the small carbon fragments in the different regions of the picture.

(2) Interpretation

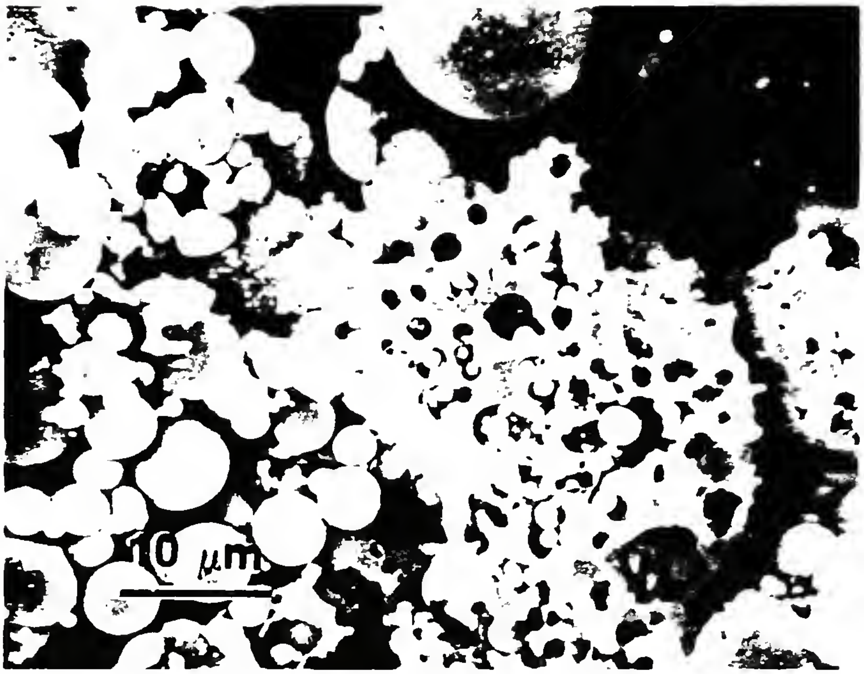
This appears to be a well-fired fly ash with smooth-textured and well-rounded particles despite its relatively coarse size distribution. The carbon residue is visible as cluster grains of sizes ranging from coarse sizes down to a few micrometers, common in nearly all fields.



LWL 1 - A Magnification: 700x.



LWL 1 - B Magnification: 3000x.



LWL 1 - C Magnification: 2000x.

LWL 1 - D Magnification: 1500x.

Results of Pozzolanic Index Test With Cement

The results of the pozzolanic index tests on this fly ash follow the same pattern as was described for the previous CPC-1 fly ash. With cement "A" there was about a 16% increase in the amount of water needed to maintain the designated flow. Samples prepared at this higher water content in the standard test method yielded strengths that were only 36% of those of the reference cement mortars. Ignoring this adjustment and preparing specimens on a 30% weight replacement basis in the supplementary tests yielded a strength of 72% of the corresponding cement mortar. The effect is somewhat less of a surprise here, because of the relatively larger increase in water demand.

Summary Characterization

This fly ash appears to be a coarse but reasonably well rounded Class F material, with an unusually low iron oxide content but otherwise unexceptional. There is a reasonably high content of residual carbon. It does increase the water demand substantially, at least in mortars, and the strength response in the standard pozzolanic index test with cement is lower than acceptable; it is much better in tests carried out without water adjustment.

DISCUSSION

The contents of this report represent a massive amount of data on a relatively large suite of fly ashes. It is thus not possible to summarize the results conveniently in the scope of a brief discussion, and easy generalizations are not possible.

Nevertheless, certain common patterns of results are reflected in the data, and do provide a basis for interpretation and synthesis.

With respect to the results of chemical analysis, the first evident generalization is that 12 of the 14 fly ashes would be categorized as Class F fly ashes. The only two that are not are the NIP-1A and the NIP-2 ashes, both from northwestern Indiana. This is a generalization that was not unexpected; for both economic and political reasons, there is considerable pressure on Indiana utilities to burn Indiana coal, which is bituminous in character, and which necessarily generates Class F fly ash.

The next generalization is that many, but not all, of the 12 fly ashes studied here maintain a common chemical pattern. Exceptions include the NIP-1, PSI-3, IME-1. and LWL-1 fly ashes, each of which will be discussed separately.

This common chemical pattern among the eight other Class F fly ashes is surely a consequence of their being derived from much the same coal; not only in the sense that it is bituminous coal, but that it is bituminous coal from the Illinois Basin deposits mined in Illinois, southwestern Indiana, and northwestern Kentucky. It appears that the coal deposits of this basin have a sufficiently uniform inorganic fraction that the fly ashes produced from this type of coal are highly

similar chemically.

The important parameters of the common pattern can be stated as follows:

a) A combined content of silicon, aluminum, and iron oxides very close to 90%,

b) A relatively high iron oxide proportion of this, the Fe_2O_3 content of the ash being in the range of 16 to 24%,

c) A relatively low CaO content, typically around 1 to 2%,

d) A very consistent alkali content and distribution, with K_2O contents about 2.5%, much smaller Na_2O contents (about 0.5%), and almost complete insolubilty of both kinds of alkalies. The implication is that these alkalies are primarily resident in the insoluble siliceous glass of the fly ash, and will contribute to the alkalinity of concrete pore solutions only very slowly should such fly ashes be incorporated in concrete.

e) Relatively low contents of SO_3, typically under 2%, and sometimes only a fraction of a percent.

In contrast to the relative consistency in these chemical analysis parameters, the different fly ashes show great differences in carbon content. This is to be expected, since carbon content reflects primarily the burning efficiency of the plant and is not therefore related specifically to the source of the coal.

Another significant parameter likely related to coal source is the content of magnetic particles, i.e those that can be reproducibly separated by a teflon-coated bar magnet of moderate strength. In these Illinois basin coal derived fly ashes the content of iron oxide is high, and so is the content of magnetic particles. The latter is

usually at least as high as the former, and often somewhat higher. Thus in the present suite of results, contents of magnetic particles as high as 30% are not uncommon, and for one ash the value of 40% was exceeded.

The chemistry of the NIP-1 fly ash is different from the common pattern described above in several respects, most notably the very much lower Fe_2O_3 content (5%), the low K_2O content (0.5%), and the high SO_3 content (over 3%), nearly all of which is soluble. There are other differences as well, including an unusually high SiO_2 content of almost 60%. This is a very different, and most unusual fly ash in many physical and physicochemical respects as well.

The PSI-3 ash is not nearly so different from the common pattern. Indeed, it is surprising to see that it is different at all, since the coal being burned is said to be an Indiana bituminous coal. Nevertheless the CaO content is nearly 7% instead of around 2% or less, and the combined content of SiO_2 + Al_2O_3 + Fe_2O_3 is only about 80% instead of 90%. In some respect this fly ash could be considered as nearing the borderline of the low CaO end of the Class C groups, although it definitely classifies as a Class F material.

The chemistry of the IME-1 fly ash is somewhat similar, although the fly ash itself is quite different. Here again the CaO content is around 7% and the combined SiO_2 + Al_2O_3 + Fe_2O_3 is around 80%. However in this ash the Fe_2O_3 content is exceedingly low, being only about 4%, way below the usual range. The material is also extremely coarse, and consists largely of non-spherical material.

The last variant Class F fly ash is the LWL-1 material. Here, while the combined major oxides is nearly 90%, the Fe_2O_3 content is again way down, at around 6%. There is also a much higher K_2O content than usual, almost 4%.

We have so far considered the Class F fly ashes in terms of chemical parameters and carbon contents. However, the behavior of any specific fly ash reflects many characteristics besides these chemical parameters; such things as particle size distribution, content of magnetic particles, content and type of glass, etc., are all important.

The particle size distributions are somewhat in the same category as carbon contents, in that they depend on the operating system of the plant at least as much as they do on the parent coal. Specifically, they tend to reflect the efficiency of the ash collection system, and the way it is laid out and operated. Most plants appear to have reasonably functional economizer ash separators ahead of the electrostatic precipitators; the resulting screening out of oversize particles tends to be at least fairly effective. At the other extreme, one plant sampled seemed not to have any functional economizer at all, the "fly ash" collected being so heavily contaminated with coarse economizer ash that it would be useless in concrete.

Generally speaking, except for measurement of the content of oversize material (>45 μm), the fly ash industry pays little attention to particle size distribution, and indeed such measurements are not even made in the ordinary methods of fly ash analysis. It is to be expected that the finer the fly ash, all other things being constant, the better the reactivity; but content of oversize material is only a very poor indicator of the real fineness of the ash. The importance of the relative amount of material in the finest size categories (13 to 5 μm, and especially below 5 μm) cannot be overstressed. One practical illustration in the present suite is the performance of the extremely

fine NIP-1 fly ash, which has a mean size of only 3 μm, and by far the highest result on the pozzolanic activity index test. In the standard test the fly-ash mortar made from this ash developed nearly half again as much strength as the reference cement mortar.

The other important parameter usually neglected is the content of magnetic particles. Our results indicate that this is frequently higher than the iron oxide content itself. The x-ray patterns of the separated magnetic fractions usually indicate traces or minor contents of quartz and mullite present as well as the well-crystallized iron oxides; furthermore, there is usually very little indication of glass present in these particles. The magnetic particles being thus composed almost entirely of material incapable of reaction with cement, one cannot expect that they will contribute substantially to any strength gain in the concrete.

Since the content of such magnetic particles in different fly ashes may be as little as 5 or 10%, or as much as (in one case) 40%, it is desirable to know the content in any given fly ash. For most of our Class F fly ashes derived from Illinois basin coals, the content is high, averaging about 25%.

These results suggest that there is good reason for considering that an appreciable portion of many fly ashes will act as fine aggregate in the concrete rather than as a cementitious component. It thus appears entirely appropriate to design mixes with a greater addition of fly ash than the content of cement to be left out of the mix, as is becoming the general practice.

Of the 14 fly ashes collected and studied in this program, only two were classified as Class C fly ashes, both from NIPSCO plants in northwestern Indiana. These have not been discussed with the others,

because of the extremely different characteristics they display.

Both of these are very high calcium fly ashes, with CaO contents of over 30%. Thus they belong in the "high calcium" end of the Class C type, and would be considered as "hot" materials. The two ashes differ considerably from each other. The NIP-1A ash has a very high carbon content, well over 8%. This is unusual for a Class C fly ash; most of these are currently being produced in new plants under excellent burning conditions and tend to have carbon contents under 1%. The other Class C ash, NIP-2, did indeed have an extremely low carbon content, less than 0.2%.

The iron oxide contents of both of these fly ashes are fairly low, around 10%, as was the content of magnetic particles. The NIP-2 ash has a difficulty in that the MgO content is extremely high, almost 11%. Enough of the analytical MgO content actually exists in the form of crystalline MgO to show clearly in the x-ray diffraction pattern, and one would have to be concerned about possible soundness problems with concrete incorporating this particular fly ash.

The results of the pozzolanic index testing with these two fly ashes were quite a bit less spectacular than might be expected from the general notion current that high-calcium Class C fly ashes are exceeding rapid reactors in concretes and generally develop very high strengths. Indeed, the results of the standard test with NIP 1-A were unsatisfactory by the conventional requirement, perhaps due to the high content of carbon in this ash. The modified testing gave a more satisfactory result. The NIP-2 ash gave quite satisfactory results in both tests (around 90% in the standard testing), but even these results were certainly not extraordinary.

To sum up, it appears from the results of this testing program that Indiana fly ashes are mostly Class F ashes, the majority of which are derived from local Illinois basin coals and have a very consistent chemistry. Some Class F fly ashes, presumably being produced from other coals, have somewhat different chemical patterns, usually showing less iron, sometimes significantly more calcium, and in one case significantly more alkalies.

The two Class C ashes we found are both are produced in the northwest corner of the state, and this seems to be part of a geographical pattern. They are both very high calcium ashes, entirely different from the Class F fly ashes in many respects.

The fly ashes in Indiana, like others elsewhere, were found to vary considerably in carbon content and in particle size distribution. Both of these properties are related as much or more to the plant conditions than to the parent coal. Should plant operating conditions change, these characteristics would change as well.

Most of the fly ashes studied would be expected to be at least marginally satisfactory in concrete, a few borderline, and at least one completely unsatisfactory. There is one Class F ash, the NIP-1, that appears to be outstanding in nearly all of its characteristics and should make excellent concrete. There is one Class C ash, the NIP-2, that seems satisfactory in all respects except for a very high content of MgO. This fly ash would need to be tested rigorously for possible development of unsoundness in concrete before it is used.

The discussion so far has been concerned with the properties of the fly ashes studied in this project. In addition to the specifics of the results obtained, contributions have been made in the project toward the methodology of studying fly ash. The following procedures used in this

project are new, so far as we know, and represent definite advantages over what had been available previously:

1. The method for accurately and reproducibly determining the content of magnetic particles in fly ash.

2. The method for specimen mounting of fly ash for scanning electron microscopy.

3. The method for analyzing and displaying the results of particle size distribution determinations to bring out meaningful differences among different fly ashes.

These represent distinct contributions to the field that may be of considerable future importance.

CONCLUSIONS

Fourteen fly ashes, representing more than 30 potentially available, have been extensively studied and characterized so as to provide a representative picture of the fly ashes currently available in Indiana. The following conclusions are drawn from these examinations:

1. Nearly all currently-produced Indiana fly ashes are low calcium Class F fly ashes; the only two high calcium Class C ashes found were both from northwestern Indiana.
2. Most of the Class F fly ashes produced in Indiana are derived from the burning of local Illinois basin bituminous coals. These fly ashes show a very consistent chemical pattern, which includes:
   - (a) high contents, ca. 90%, of combined $SiO_2 + Al_2O_3 + Fe_2O_3$,
   - (b) high iron oxide contents, ranging from about 16% to about 24%, and correspondingly large contents of magnetic particles,
   - (c) low CaO contents, typically 2% or less,
   - (d) consistent alkali contents and distributions, with K_2O contents of about 2%, roughly 5 times the Na_2O contents, with both forms of alkali essentially insoluble, and
   - (e) contents of SO_3 no more than about 2%.
3. About a third of the Class F fly ashes were different in chemistry, presumably due to other coal being burned. some of the differences included significantly higher CaO contents, significantly lower iron contents, and in one case a

substantially higher alkali content.

4. The fly ashes of Indiana were found to vary greatly in content of unburned carbon. A number were found to be exceedingly low in this parameter, substantially under 1%; others were as high as 9%.
5. Particle size distributions were also found to be very different. One exceedingly fine fly ash was found, with a mean particle diameter of 3μm, and would appear to be exceptionally beneficial in concrete; one exceedingly coarse ash had a mean particle diameter of 78μm, and would seem to be entirely unusable in concrete.
6. The two Class C fly ashes were both of very high CaO content. Their characteristics differed significantly from the Class F fly ashes, and to some extent from each other.
7. The magnetic particle contents of many of the fly ashes were high, and the particles consisted almost entirely of crystalline components that are not reactive with cement. Such particles constitute addition to the fine aggregate rather than replacement of cement.
8. New methods of study of fly ashes developed in this project include a method of accurately and reproducibly determining the content of magnetic particles; an improved method of mounting fly ash for observation in scanning electron microscopy; and a procedure for displaying the results of particle size distribution measurements for easy and consistent interpretation.

COVER DESIGN BY ALDO GIORGINI